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Methods of Analysis for By-Product PCBs-Literature Review and Preliminary Recommendations

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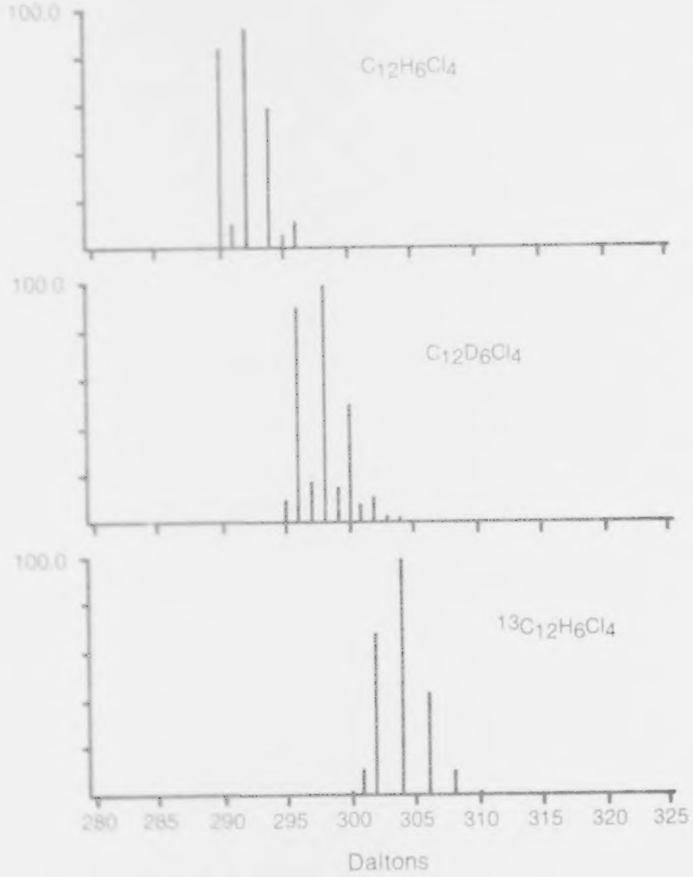

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16. ABSTRACT

A review of the literature on polychlorinated biphenyl (PCB) analysis and recommendations for methods to determine by-product PCBs in commercial products and other matrices is presented. This report was prepared to assist EPA in formulating a rule regulating by-product PCBs. The published literature on PCB analysis is critically reviewed. Several hundred references are cited in a bibliography. The review if subdivided into extraction, cleanup, determination, data reduction, confirmation, screening, quality assurance, and by-product analysis sections. The determination section includes TLC, HPLC, GC (PGC and CGC), GC detectors (ECD, FID, HECD, EIMS, and other MS) and nonchromatographic analytical methods (NMR, IR, electrochemistry, NAA, and RIA). Techniques applicable to analysis of commercial products, air, and water for by-product PCBs are discussed. The final section of this report presents a recommended overall primary analytical scheme.

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METHODS OF ANALYSIS FOR BY-PRODUCT PCBs--LITERATURE REVIEW AND PRELIMINARY RECOMMENDATIONS

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Washington, DC 20460

Attn: Dr. Frederick W. Kutz, Project Officer
Mr. David P. Redford, Task Manager

PREFACE

This report presents the results of a literature review and preliminary methods recommendations accomplished on MRI Project No. 4901-A, Task 51, "PCB Analytical Methodology Task," for the Environmental Protection Agency (EPA Prime Contract No. 68-01-5915). The review was performed and the document prepared by Drs. Mitchell D. Erickson and John S. Stanley, with assistance from Elliot Hirsch, Scott Meeks, Betty Jones, Kay Turman, Kathy Funk, Lanora Moore, Cindy Melenson, Carol Shaw, and Gloria Sultanik.

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LIST OF TERMS, ABBREVIATIONS, AND SYMBOLS

Accuracy	Closeness of analytical result to "true" value.
Aroclor	Trade name (Monsanto) for a series of commercial PCB mixtures marketed in the United States.
Askarel	Nonflammable synthetic chlorinated hydrocarbon insulating liquids used in capacitors, transformers, etc.; often containing PCBs.
By-product PCBs	PCBs generated as by-products or impurities in synthesis of other products (as opposed to commercial PCBs).
CGC	Capillary column gas-liquid chromatography (includes WCOT, SCOT, fused silica, glass, and metal).
CI	Chemical ionization (mass spectrometry).
CIMS	Positive chemical ionization mass spectrometry.
Congener	One of 209 PCBs, not necessarily the same homolog.
Cutoff	Lowest PCB concentration of regulatory concern.
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene.
DDT	1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane.
ECD	Electron capture detector.
EI	Electron impact ionization (mass spectrometry).
EIMS	Electron impact mass spectrometry.
Equivalent method	Any method, certified against the primary method, which can be used for routine analysis of samples. Also, termed screening method.
External standard	Standards for calculation not added to the sample extract.
FFAP	Free fatty acid phase.

FID	Flame ionization detector.
FTIR	Fourier transform infrared spectrometry.
GC	Gas-liquid chromatography (column type unspecified).
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified).
GPC	Gel permeation chromatography.
HECD	Hall electrolytic conductivity detector (other similar detectors such as the Coulson are included).
HEETP	Height equivalent to an effective theoretical plate.
Homolog	One of the 10 degrees of chlorination of PCBs ($C_{12}H_9Cl$ through $C_{12}Cl_{10}$).
HPLC	High performance liquid chromatography.
HREIMS	High resolution electron impact mass spectrometry.
Internal standard	Standards used expressly for quantitation added to sample extract immediately prior to the analytical determination.
IR	Infrared spectrometry.
Isomer	One of up to 46 PCBs possessing the same degree of chlorination (3,4- and 4,4'-dichlorobiphenyl are different isomers).
KOH	Potassium hydroxide.
LMS	Limited mass scanning (mass spectrometry).
LOD	Lower limit of detection (also MDL). Lowest concentration which an analyte can be identified as present in the sample at a stated statistical confidence level.
LOQ	Lower limit of quantitation. Lowest concentration to which a value can be assigned at a stated statistical confidence level.
MDL	Method detection limit.
Mean	Arithmetic mean.
MS/MS	Mass spectrometry/mass spectrometry.
m/z	Mass-to-charge ratio.

NAA	Neutron activation analysis.
NCI	Negative chemical ionization (mass spectrometry).
NCIMS	Negative chemical ionization mass spectrometry.
NMR	Nuclear magentic resonance spectrometry.
PBB	Polybrominated biphenyl.
PCB	Polychlorinated biphenyl (including monochlorobiphenyl, but excluding biphenyl).
PCN	Polychlorinated napthalene.
PCT	Polychlorinated terphenyl.
PGC	Packed column gas-liquid chromatography.
ppb	Parts per billion (10^{-9}).
ppm	Parts per million (10^{-6}).
Precision	Reproducibility of an analysis, measured by SD of replicates.
QA	Quality assurance. An organization's program for assuring the integrity of data it produces or uses.
QC	Quality control. The specific activities and procedures designed and implemented to measure and control the quality of data being produced.
Remand Rule	Rulemaking for new PCB regulations for inclusion in 40 CFR, Part 761 in response to orders from the U.S. Court of Appeals from the District of Columbia on October 30, 1980 and April 13, 1981.
RI	Retention index.
RIA	Radioimmunoassay or radio isotope dilution assay.
RIC	Reconstructed ion chromatogram.
RMR	Relative molar response.
RSD	Percent relative standard deviation (SD/mean x 100).
SCOT	Support coated open tubular (CGC column).

SD	Standard deviation.
Sensitivity	The slope of instrument response with respect to the amount of analyte. Also used colloquially in reference to lowest detectable amount of analyte.
SIM	Selected ion monitoring (also mid or mass fragmentography).
Surrogate	Standard compounds added to the sample prior to any analytical manipulations for the express purpose of measuring recovery through extraction, cleanup, etc.
TCD	Thermal conductivity detector.
TCDD	Tetrachlorodibenzo-p-dioxin.
TIC	Total ion current chromatogram.
TLC	Thin-layer chromatography.
WCOT	Wall coated open tubular (CGC column).

SECTION 1

SUMMARY

The published literature on PCB analysis is critically reviewed. Several hundred references are cited in a bibliography. The review is subdivided into extraction, cleanup, determination, data reduction, confirmation, screening, quality assurance, and by-product analysis sections. The determination section includes TLC, HPLC, GC (PGC and CGC), GC detectors (ECD, FID, HECD, EIMS, and other MS) and nonchromatographic analytical methods (NMR, IR, electrochemistry, NAA, and RIA).

Based on the review of the literature, personal communications with researchers in the field, and the authors' judgment, techniques applicable to analysis of commercial products, air, and water for by-product PCBs under the Remand Rule are discussed. Each individual analytical component (extraction, cleanup, determination, etc.) is separately discussed. The final section of this report presents the recommended overall primary analytical scheme:

1. Homogenize sample and subsample if necessary.

2. Incorporate surrogate compounds (e.g., four ^{13}C PCB congeners).

3. Dilute, extract, or clean up as required.

4. Concentrate or dilute to a known volume.

5. Analyze a known aliquot by GC/EIMS.

6. Identify PCBs by relative retention time and mass spectral characteristics.

7. Integrate the PCBs by homolog and calculate amounts of each homolog by normalizing the responses to responses for the surrogate compounds, using one or more homolog response factors.

8. Sum all 10 homolog concentrations to obtain a total PCB value.

9. Report on standard reporting form.

10. Follow specified routine QC (blanks, controls, duplicates, standard condition, instrument performance criteria, etc.).

11. Maintain appropriate records.

Several details in this scheme are subject to revision, as discussed in the report. Several unresolved issues are discussed, including the permissible flexibility in the method, the use of equivalent methods, and quality assurance.

SECTION 2

INTRODUCTION

PCBs have been manufactured as commercial products since 1929 and marketed under trade names such as Aroclor (United States), Chlophen (Germany), and Kanechlor (Japan). These were all complex mixtures of many congeners and several homologs. They were used as dielectric fluids in capacitors and transformers, hydraulic fluids, fire retardants, plasticizers, and many other applications. Their manufacture and use have been frequently reviewed (Hutzinger et al., 1974; and many other reviews listed in "Review Articles on PCBs" section below).

Beginning in 1966 (Jensen, 1972; anonymous, 1966), PCBs were found in environmental samples as interferents with chlorinated pesticides (e.g., DDT) analysis with increasing frequency. As the magnitude of the problem grew, the emphasis on PCBs gradually shifted from interferents to analytes. Concomitantly, their toxicology was being studied. While their toxicity varies among isomers and species, PCBs have been sufficiently implicated in animal and human toxicity to warrant their ban in the United States (Toxic Substances Control Act (TSCA), Public Law 94-469, October 11, 1976). The public outcry prior to TSCA and enforcement of the law thereafter have prompted increased scientific interest in all aspects of PCBs.

Central to the environmental studies of PCBs is their analysis. Most of the early methods were direct adaptations of chlorinated pesticide procedures. As interest grew, analytical techniques improved and methods of analysis became increasingly sophisticated. However, PCB analysis is plagued by the fact that PCBs are not one specific compound like most pesticides, but in fact are a class of 209 congeners. Until very recently, all of the PCB analyses were directed toward commercial (e.g., Aroclor) products or their derivatives (metabolites, weathered samples, etc.). The complexity of the raw data (chromatograms) and lack of other standards have led scientists to report PCB findings in terms of Aroclor (or other products) calibration standards. This procedure is at best approximate when the sample resembles the standard and becomes hopeless if the sample does not "match" standards.

The problem of PCB analysis has recently become more complex due to concern over incineration products and by-product PCBs, where the PCB mixture in no way resembles an Aroclor pattern. Incinerator products are of concern since U.S enforcement efforts have recently concentrated on destruction of existing PCB products rather than on landfill disposal. The concern over by-product PCBs may be traced to the opinion of U.S. courts that PCBs generated as impurities in other products are subject to the TSCA ban on PCB manufacture.

This document presents a review of analytical techniques used for the analysis of PCB and discusses which of these may be applicable to determination of by-product PCBs. A general analytical scheme is proposed with several options in areas where there is no clear best available technology.

SECTION 3

LITERATURE REVIEW

This section is a critical review of the published literature on analytical techniques for PCBs. Where possible, comments have been made regarding the quality of the work and the utility of the technique. However, discussion of the relevance of techniques toward the PCB Remand Rule has been left to Sections 4 and 5.

SOURCES OF INFORMATION

Computerized and manual searches and relevant references in recent articles were used. Many documents were obtained from the personal files of MRI employees. Recent issues of several key journals (*Analytical Chemistry*, *Journal of Chromatography*, *Journal of the Association of Analytical Chemists*, *Environmental Science and Technology*, etc.) were searched manually to pick up any recent references not yet in the computer data bases. In addition, several known PCB researchers (Appendix A) were called to discuss approaches to the Remand Rule. In these discussions, they were asked to send copies or give references to any recent publications or preprints.

The computer searches were done using DIALOG. *Chemical Abstracts* (CA) files were searched back to 1972, printing all references containing "PCB" and synonyms and keywords beginning with the following letters: "anal," "chromatogr," "mass spectr" and synonyms. A similar search was performed on the National Technical Information Service data base (now including Smithsonian Science Information Exchange). These searches printed out 349 citations, of which 188 were judged sufficiently relevant to obtain at least the CA abstract. In addition to nonanalytical articles, articles where PCBs were mentioned but were clearly not the major focus of the article, and articles which clearly contained only analytical results and not methods, the majority of citations not obtained were in obscure foreign language journals and apparently were similar to other available references.

Once the primary search data had been digested, it became apparent that several authors were of primary interest and all of their recent (1980 and 1981) publications were retrieved by a CA search on their name. These authors were P. W. Albro, T. F. Bidleman, U. A. Th. Brinkman, O. Hutzinger, R. G. Kaley, S. Safe, D. L. Stalling. Most of the new citations retrieved by this search were irrelevant (metabolism studies, synthesis, etc.) to this report.

An additional manual cross-check was made with the document "Polychlorinated Biphenyls, Polybrominated Biphenyls, and Their Contaminants: A Literature Compilation 1965-1977" (Winslow and Gerstner, 1978). This document contains 1,880 PCB citations, although not all pertain to analytical methods.

References contained in review articles and primary literature were also checked to assure that no important articles were missed by the computer search. Several articles were added to the files by these searches.

REVIEW PROCEDURE

All articles cited in the bibliography (Appendix B) were surveyed for relevant analytical details. The salient features of each article were noted and any key subject areas were listed. Each citation was cross filed in any of 33 applicable key subject areas (PGC, CGC, EIMS, Review, etc.).

REVIEW ARTICLES ON PCBs

Any class of chemical compounds as often studied and as subject to regulatory pressure as PCBs has been the subject of review articles. A total of 27 books and articles were characterized as PCB reviews. The PCB review most often cited is probably the book The Chemistry of PCBs by Hutzinger et al., (1974). This book characterizes commercial PCBs; synthesis routes; chemical and photochemical reactions; metabolism; mass spectrometry; NMR, UV, and IR spectral properties; determination methods, and recent developments. Although dated, this review covers the general subject and the analysis of PCBs (in 1974) comprehensively.

Reynolds (1969) reviewed the problems of PCB interference with the analysis of pesticide residues and later expanded on this in Residue Reviews (Reynolds, 1971). Risebrough (1971) reviewed analytical techniques for PCBs in environmental samples. Fishbein's (1972) review of the chromatographic and biological aspects of polychlorinated biphenyls discussed column chromatography, TLC, GC, and GC/EIMS in some detail. DeVos (1972) reviewed the methods for pesticides and PCBs in wildlife samples used by various laboratories in the Netherlands. Lincer (1973) reviewed PCBs, again as interferents with pesticide residue analysis. Safe (1976) reviewed the analytical problems and methods for PCBs as part of a national conference on PCBs (Ayer, 1976) which covered all aspects of the PCB issue (biology, metabolism, destruction, regulatory, etc.).

Sherma (1975) reviewed GC of PCBs, including extraction, cleanup, GC systems, identification, confirmation, and quantitation. Chau and Sampson (1975), in an attempt to standardize quantitation, surveyed and reviewed the various methods for PGC/ECD quantitation. Lao et al. (1976) reviewed the application of GC/MS to PCB analysis. Extraction, chromatographic separation (cleanup), GC/ECD, and computer-aided data interpretation were discussed by Krull (1977). Brinkman et al. (1978) discussed various literature procedures for discrimination between PCBs and polychlorinated naphthalenes (PCN). Lawrence and Turton (1978) included PCBs in a tabulation of HPLC data for 166 pesticides.

Environmental Health Perspectives devoted an entire issue (Rall, 1978) to PCBs. Pomerantz et al. (1978) reviewed the chemistry of PCBs; Matthews et al. (1979) reviewed metabolism and toxicity; Cordle et al. (1978) reviewed human exposure; Kimbrough reviewed animal toxicology; and the DHEW Subcommittee of Health Effects of PCBs and PBBs (1978a, 1978b) provided general recommendations and general summary and conclusions which included discussions of the analytical aspects of PCBs.

Stalling et al. (1979) reviewed PCB analysis with particular emphasis on their own work of automating the extraction and cleanup processes.

The sampling and analysis of PCBs in air have been reviewed by Lao et al. (1976), Margeson (1977), and Fuller et al. (1976).

The analytical aspects of PCBs have also been reviewed by Sherma (1981), Nose (1976), and Tanabe (1973). Finlay et al. (1976) reviewed PCB levels in the environment but did not discuss analysis. Other reviews not discussing analysis include Resource Planning Commission (1982), Fishbein (1979), and Kimbrough (1980).

None of the review articles discussed above is current (the most recent was 1979), nor do they discuss the problems of determination of incidentally generated PCBs. In response to the PCB Remand Rule, the Chemical Manufacturers Association (1981) critically reviewed the PCB analytical techniques potentially applicable to the rule and recommended that GC/EIMS be the method of choice for analysis under this rule.

STANDARD METHODS

Table 1 lists the standard analytical methods available for PCBs. It should be noted that not all of the methods listed are sanctioned at this point. Many have interim status and some have been proposed but never endorsed by an organization. The standard methods provide analytical approaches for the measurement of PCBs in a variety of materials including water, wastewaters, soils, sediments, sludges, air, combustion and incinerator emissions, capacitor askarels, transformer fluids, waste oils, mixtures of chlorinated benzenes, pigments, food, milk, and adipose tissues.

Table 1 summarizes each of the standard methods. Extraction and cleanup procedures are presented in terms of the materials and reagents required for analysis. Less than half of the methods comment on the criteria required to make qualitative determinations for the presence of PCBs in sample extracts. The method of quantitation for each of the analysis schemes is presented along with the limit of detection (LOD), if specified. Additional analytical procedures to confirm the levels or presence of PCBs are also indicated. More than half of the standard methods mention quality assurance in some respect. The quality assurance steps include analysis of blanks, replicates, control samples, spiked additions, and accuracy, precision, and instrumental performance criteria.

All of the methods, except those provided by DCMA (1981) and Dow (1981) are directed to the analysis of PCBs as Aroclors or similar mixtures. The DCMA (1981) and Dow (1981) methods were developed for the analysis of byproduct PCBs in commercial products.

TABLE 1. STANDARD METHODS OF ANALYSIS FOR PCBs

Method	Matrix	Extraction	Cleanup	Determination method	Qual.	Quant. method	LOD	Confirmation	QA	Reference
ANSI	Air (toluene impinger)	-	(H_2SO_4) (Saponification) (Alumina)	PGC/ECD	No	Single peak	2 ppb	None	Yes	ANSI, 1974
ANSI	Water	Hexane	(H_2SO_4) (Saponification) Alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	None	Yes	ANSI, 1974
ANSI	Sediment soil	CH_3CN/ hexane	H_2SO_4 Saponify/ alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	None	Yes	ANSI, 1974
AOAC (29)	Food	CH_3CN/Pet. ether	Florisil MgO/ Celite saponification	PGC/ECD	No	Total area or Ind. peaks	NS[a]	TLC paper chrom.	No	AOAC, 1980a AOAC, 1980b
	Paper and paperboard	saponification								
D3303-74	Capacitor Askarels	DI[b]	None	SCOT CGC/FID	No	Total area	2.8×10^{-8} mol/ℓ	None	No	ASTM, 1980a
D3304-74	Air	DI		PGC/ECD	No	Total area	NS	None	Yes	ASTM, 1980b
	Water Soil, sediment	Hexane H_2O/CH_3CN	(H_2SO_4) (Saponification) (alumina)							
DCMA	3 pigment types	A. Hexane/ H_2SO_4 B. CH_2Cl_2	None Florisil	PGC/ECD	No	10 isomers	~ 1 ppm/homolog	PGC/MS	Yes	DCMA, 1981
Devenish	Water	Hexane	Alumina	PGC/ECD	No	NS	106 ng/ℓ	None	No	Devenish and Harling-Bowen, 1980
DOW	Chlorinated benzenes	DI	None	PGC/EIMS	Yes	Total peak height/ homolog	NS	None	Yes	Dow, 1981
EPA (Halocarbon)	Sludge	Hexane/ CH_2Cl_2/ acetone (83/15/2)	GPC S removed	PGC/ECD	Yes	Peak area or peak height	NS	GC/MS	Yes	Rodriguez et al., 1980
EPA (PP)	Sludge	CH_2Cl_2 (base/ neutral and acid fractions)[c]	GPC	PGC/EIMS	Yes	NS	NS	None	Yes	EPA, 1979e
EPA (304h)	Water	Hexane/ CH_2Cl_2 (85/15)	Florisil/ silica gel (CH_3CN) (S removal)	PGC/ECD or HECD	Yes	Summed areas or or Webb-McCall	NS	None	Yes	EPA, 1978
EPA (B100)	Sludge	CH_2Cl_2 (3 fractions)	GPC Silica gel	CGC/EIMS or PGC/EIMS	Yes	NS	NS	None	Yes	Ballinger, 1978

(continued)

TABLE 1 (continued)

Method	Matrix	Extraction	Cleanup	Determination method	Qual.	Quant. method	LOD	Confirmation	QA	Reference
EPA (HERL)	Milk	Acetone/ hexane	CH_3CN Florisil Silica acid	PGC/ECD	Yes	Ind. peaks	50 ppb	Perchlorination	Yes	Watts, 1980 Sherma, 1981
EPA (HERL)	Adipose	Pet. ether/ CH_3CN	Saponification Florisil	TLC	No	Semiquant.	10 ppm	None	No	Watts, 1980
EPA (oil)	Transformer fluids or waste oils	DI	(H_2SO_4) (Florisil) (Alumina) (Silica gel) (GPC), (CH_3CN)	PGC/HECD or /ECD or /EIMS (CGC)	No	Total area or Webb-McCall	1 mg/kg	None	Yes	EPA, 1981 Bellar and Lichtenberg, 1981
EPA (gas)	Natural gas sampled with Florisil	Hexane	H_2SO_4	PGC/ECD		Total area peak height or Webb-McCall (Perchlorination)	0.1-2 $\mu g/m^3$	None	No	Harris and Mitchell, 1981
608	Water	CH_2Cl_2	(Florisil) (S removal)	PGC/ECD	No	Area	0.04-0.15 $\mu g/\ell$	None	Yes	EPA, 1979a
625	Water	CH_2Cl_2	None	PGC/EIMS (CGC)	Yes	Area	NS	None	Yes	EPA, 1979b
EPA (stack)	Incinerator emissions and ambient air collected on Florisil	Hexane	(H_2SO_4)	Perchlorination PGC/ECD	No	Area	10 ng	GC/MS	No	Haile and Baladi, 1977
EPA	Combustion sources collected on Florisil	Pentane or CH_2Cl_2	(Florisil/ silica gel)	PGC/MS	Yes	Area/ homolog	0.1 ng/inj	None	No	Levins et al., 1979
NIOSH (air) (P&CAM 244)	Air collected on Florisil	Hexane	None	PGC/ECD	No	Peak height or area from standard curve or Webb-McCall	0.01 mg/m^3	None	No	NIOSH, 1977a
NIOSH (air) (P&CAM 253)	Air collected on Florisil	Hexane	None	PGC/ECD Perchlorination	No	Peak height or area from standard curve	0.01 mg/m^3	Perchlorination	No	NIOSH, 1977b
Japan	Food	Several	Silica gel Saponification (Florisil)	PGC/ECD	Yes	Summed areas perchlorination	NS	None	No	Tanabe, 1976
PAM	Food	CH_3CN/Pet. ether	Silicic acid (Saponification) (Oxidation) (Florisil)	PGC/ECD (PGC/HECD) (NP-TLC) (RP TLC)	No	Area	NS	TLC	No	FDA, 1977

a No specific details.

b Direct injection.

c Techniques in parentheses are described as optional in the protocol.

The ANSI methods are based on techniques that were used by the Monsanto Industrial Chemical Company for the isolation and determination of PCBs in water, soil, sediment, and biological materials. Packed column gas chromatography with electron capture detection (PGC/ECD) is the designated method for quantitation of PCBs as Aroclors in the ANSI methods. Mass spectrometry, however, is recommended for each of the designated analysis schemes if confirmation is required. The cleanup techniques are required only if interferences are noted for the PGC/ECD determination. The quality assurance procedures in the ANSI methods emphasize the number of theoretical plates and tailing factor for the packed gas chromatography column.

The ASTM, AOAC, and EPA methods are generally designed for a particular matrix. The level of quality assurance procedures varies from method to method. The recent methods provide quality assurance programs of greater detail and require reasonable effort to maintain the accuracy and precision of the overall determination.

The EPA method for analysis of PCBs in transformer oils and crude oils provides the most generalized approach with respect to sample preparation, cleanup procedures, and instrumental analysis. Several cleanup procedures are provided as optional approaches in this protocol, and instrumental analysis by halogen specific, electron capture, or mass spectrometry detectors are allowed, provided appropriate limits of detection can be achieved. A strong quality assurance program including control samples, daily quality control check samples, blanks, standard additions, accuracy and precision records, and instrumental and chromatographic performance criteria is required to support all data generated by the method.

The Dow (1981) and DCMA (1981) procedures also require strong quality assurance programs for analysis of by-product PCBs.

SAMPLING

The first step in any successful analysis is the collection of representative samples. The selection of sampling sites, frequency of sampling, number of samples, measurement of physical and chemical parameters of the sample, and the overall statistical design of sampling methods have been provided in extensive detail (Moser and Huibregtse, 1976; EPA, 1976). The sampling design in most cases is directly related to the objectives of a specific research program as a regulatory action.

The methods that are of interest in the context of this report are the procedures practiced for obtaining representative specimen of air, water, and solids. Aqueous and solid media are generally collected as grab samples, although aqueous samples have been preconcentrated on solid adsorbents prior to extraction.

Water Sampling

The solid adsorbents used for aqueous preconcentration methods include macroreticular resins (Coburn et al., 1977; Seiber, 1974; Musty and Nickless, 1974; Webb, 1975; Picer and Picer, 1980), polyurethane foam and Chromosorb W coated with a mixture of undecane and Carbowax 4000 monostearate (Gesser et al., 1971; Lawrence and Tosine, 1976; Bellar and Lichtenberg, 1975; Ahling and Jensen, 1970; Osterroht, 1974; Musty and Nickless, 1976), as well as Tenax (Leoni et al., 1976). Preconcentrating organic analytes from aqueous media allows the analyst to work with large volumes of water and thus lowers the method detection limit for the compounds of interest. The sorbent preconcentration method also can be used as a continuous on-site sampling procedure.

Air Sampling

The PCBs in ambient air and flue gas emissions have been collected on solid adsorbents including polyurethane foam plugs, Tenax, XAD-resins, Florisil, Chromosorb, and Poropak and combinations of these materials (Bidleman and Olney, 1974; Bidleman et al., 1980; Bidleman, 1981; Bidleman et al., 1981; Billings and Bidleman, 1980, 1982; Burdick and Bidleman, 1981; Simon and Bidleman, 1978, 1979; Lewis et al., 1977a, 1977b; Lewis and MacLeod, 1982; Lewis and Jackson, 1982; Williams et al., 1980; Haile and Baladi, 1977; Giam et al., 1975; Haile et al., 1982; Stanley et al., 1982; Harris and Mitchell, 1981). The solid adsorbents are effective for sampling PCBs in air although some problems have been encountered with breakthrough of the lower molecular weight PCBs at high flow rates for extended sampling periods.

Doskey and Andren (1979) evaluated polyurethane foam coated with DC 200, Florisil, and Amberlite XAD-2 resin for their ability to sample airborne PCBs. The collection efficiency of the adsorbents was studied using carbon-14 labeled 2,5,2',5'-tetrachlorobiphenyl. The XAD-2 resin was found to have an excellent collection efficiency for the tetrachlorobiphenyl at a flow rate of 1 liter/min. Their sampling system yielded 96.5% collection efficiencies for the tetrachlorobiphenyl and 83.0% for Aroclor 1221. Further investigations demonstrated low retention efficiencies for monochlorobiphenyl (72%) and dichlorobiphenyl (86%), thus demonstrating that the sampling system was not equally effective for all PCB congeners. The analytical recoveries for tetrachlorobiphenyl, Aroclor 1242, and Aroclor 1221 were 85.5%, 80.1%, and 64.9%, respectively.

Hanneman (personal communication, 1982) reported that PCBs were not retained at acceptable levels on common solid adsorbents when the flue gas temperature was greater than 150°C or in cases where the air contained an aerosol of a nonpolar material in which PCBs are very soluble. Hanneman reported successful collection of PCBs in these instances using polyurethane foam plugs coated with liquid polydimethylsilocane. Several plugs of the coated polyurethane were placed in a water-cooled jacket to sample the air at elevated temperatures. A PCB isomer was added to the surface of the foam plugs as a surrogate prior to sampling. A second PCB isomer was added to the foam plugs after sampling to monitor surrogate recovery and collection efficiency.

EXTRACTION

Reliable PCB analysis begins with the quantitative extraction of the analytes from the sample matrix. The extraction method is dependent on the sample type and the complexity of the matrix encountered. In general, the extraction methods require the use of solvents such as petroleum ether, hexane, methylene chloride, acetone, and acetonitrile. Digestion of the sample matrix with sulfuric acid or saponification with alcoholic potassium hydroxide is necessary in some instances to effectively extract incorporated PCBs. Dilution with suitable organic solvents prior to gas chromatography and even direct injection of some PCB-contaminated samples have provided suitable quantitative analysis. PCBs in air and flue gas emissions are typically collected on solid adsorbents and removed by extracting with a suitable solvent.

Standard Methods

A number of standard extraction methods for specific sample types are listed in Table 1. The standard methods include extraction techniques for transformer and capacitor oils, food, soils, sediments, dyes, milk, adipose tissue, sludge, wastewater, natural waters, emissions from combustion sources, and ambient air.

Review Articles

Extraction methods have been reviewed previously (Hutzinger et al., 1974; Sherma, 1975; Krull, 1977). Factors and problems that should be considered for a given extraction procedure (Albro, 1979) include the following: (a) each extraction method must be validated for each different matrix; (b) the nature of the sample matrix influences the effectiveness of a given extraction procedure through various matrix properties. These properties include the solubility of the matrix in solvent, the ease of homogenizing the sample for subsampling, the water content of the sample which greatly affects the extraction efficiency of the solvent, and the lipid content of tissue samples that governs the volume of solvent required for quantitative extraction; and (c) the incorporation of the analyte in a sample matrix and the most effective means of adding spikes to the sample for method evaluation and quality assurance measurements.

Primary Literature

A large number of extraction techniques provide quantitative recovery of PCBs from widely different matrices. The application of the various extraction procedures to specific sample types is discussed below.

Air--

Simple and straightforward extraction procedures are used for extraction of adsorbents from air sampling. Ambient air and flue gas emissions have been collected on adsorbents including polyurethane filter plugs (Bidleman and Olney, 1974; Bidleman et al., 1980; Bidleman, 1981; Bidleman et al., 1981; Billings and Bidleman, 1980, 1982; Simon and Bidleman, 1977a, 1977b, 1977c; Lewis and MacLeod, 1982; Lewis and Jackson, 1982), Florisil (Harris and Mitchell, 1981; Williams et al., 1980; Haile and Baladi, 1977; Giam et al., 1975), and Amberlite XAD-2 resin (Haile and Lopez-Avila, 1981; Stanley et al., 1982). PCBs were quantitatively recovered from these adsorbent materials via extraction with hexane, petroleum ether or benzene in a Soxhlet apparatus or as small chromatographic columns.

Water and Wastewater--

PCBs in aqueous samples, including natural waters, potable supplies, sewage effluents and industrial wastewaters, have been extracted by a number of procedures. Liquid-liquid extraction with hexane, cyclohexane or methylene chloride provide quantitative isolation of PCBs from aqueous samples (Brownrigg et al., 1974; Devinish and Harling-Bowen, 1980; EPA, 1979a, 1979b; Haque et al., 1974; Adams et al., 1979; Bellar and Lichtenberg, 1975; Caragay and Levins, 1979). In principle it is possible to extract all PCBs present in any water sample without large scale solvent extraction (Krull, 1977). Lower levels of detection of PCBs in aqueous samples have been achieved through the application of solid adsorbents for large volumes that cannot be effectively handled by classical liquid-liquid extraction procedures. The adsorbents are extracted with hexane, petroleum ether, and diethylether to recover the PCBs. Macroreticular resins (XAD-2, -4, -7, and -8) have been evaluated in a number of studies (Coburn et al., 1977; Seiber, 1974; Musty and Nickless, 1974; and Webb, 1975; Picer and Picer, 1980). Polyurethane foams and Chromosorb W coated with a mixture of undecane and Carbowax 4000 monosterate as a reversed liquid-liquid partition method have also demonstrated successful isolation of PCBs from aqueous matrices (Gesser et al., 1971; Lawrence and Tosine, 1976; Bellar and Lichtenberg, 1975; Ahling and Jensen, 1970; Osterroht, 1974; Musty and Nickless, 1976).

Two studies (Bellar and Lichtenberg, 1975; Webb, 1975) compared various extraction methods including batch liquid-liquid extraction, vortex stirring with an organic solvent, and adsorbent concentration on polyurethane and amberlite macroreticular resins. Extraction efficiencies of PCBs were greatest with liquid-liquid extraction.

Continuous liquid-liquid extractors (Leoni, 1971; Ahnoff and Josefsson, 1973, 1974; Ahnoff et al., 1979) and steam distillation of aqueous samples with simultaneous liquid-liquid extractions of the distillate into pentane (Godefroot, 1982) have been studied as alternate means to lower detection limits for specific organic compounds including PCBs present in water.

Wastewaters from some industrial processes have posed some interesting problems in measurement of total PCBs released. In particular, the cellulose fibers collected from paper mill effluents required hydrolysis with alcoholic potassium hydroxide and extraction with hexane or methylene chloride as well as extraction of the aqueous phase to effectively quantitate total PCBs (Delfino and Easty, 1979; Easty and Wabers, 1978). Dissolution of the residual fibers in paper mill effluents with 72% H_2SO_4 followed by dilution with water and extraction with hexane was demonstrated to promote quantitative isolation of PCBs.

Colenutt and Thorburn (1980) have discussed the application of gas stripping or purge and trap techniques for the analysis of PCBs in water. Spiked PCBs were removed from water samples by purging with nitrogen at ambient temperature. The PCBs were concentrated on activated charcoal and desorbed with a minimum volume (50 µl-1.0 ml) of organic solvent. Recoveries of greater than 90% were reported for Aroclors 1221, 1248, and 1254. The efficiency of this extraction technique is dependent on the gas flow rate, the time of stripping, adsorbent particle size, and the desorbing solvent.

Soils, Sediments, and Sludges--

Soxhlet extraction of soils and sediments with hexane-acetone, petroleum ether-acetone, or hexane has been a common method of isolating the PCBs (Bellar and Lichtenberg, 1975; Eder, 1976a; Goerlitz and Law, 1974; Jensen et al., 1977; Macleod, 1979; Seidl and Ballschsmiter, 1976; Adams et al., 1979; Hutzinger et al., 1974). Other methods that have been used for soils, sediments, and sewage sludges have included silica sonication (Chau and Babjak, 1979), blending with suitable solvent such as methylene chloride with centrifugation for separation of the phases (Rodriguez et al., 1980), and a column technique that required mixing sediment with Florisil and eluting with 10% water in acetonitrile. Ethanolic potassium hydroxide reflux prior to extraction of the sediment has been reported in at least one instance (Wakimoto et al., 1971).

Soxhlet extraction, solvent shakeout, solvent blending, two column elution methods, and high frequency dispersion (Tissumizer) extraction techniques were compared for the same bottom sediment (Bellar and Lichtenberg, 1975). The results indicated that the highest recovery of PCBs was achieved by Soxhlet extraction of dried samples. The authors concluded that this should be the technique of choice for bottom sediments and sludges.

Bellar et al. (1980) extended this study using Soxhlet extraction, sonification, and steam distillation for the recovery of PCBs from environmentally contaminated lake and river bottom materials. The high frequency dispersion extraction technique was not used in this study because of excessive and rapid wearing of parts of the device and excessive breakage of glassware. Bottom sediments were spiked with Aroclor 1254 and extracted by the three techniques. The mean recovery of PCBs for spiked samples was 81-109% for the different methods, indicating that any of the three might be used for quantitative extraction. However, the Soxhlet extraction method yielded higher levels of PCBs from environmentally contaminated sediments than either steam distillation or sonification. The results of this study are not conclusive since only one solid sample matrix was considered.

Seidl and Ballschmiter (1976a) studied the recovery rates of PCBs from soil using Soxhlet extraction with hexane, acetone/acetonitrile, or ultrasonic extraction with acetone. Carbon-14 labeled Clophen A-30 was added to the soil to simplify the extraction studies. The authors concluded that Soxhlet extraction with acetone/acetonitrile yielded the best recoveries (greater than 95%) and Soxhlet extraction with hexane or ultrasonic extraction with acetone was not suitable for good recoveries of PCBs from soil.

Biological Matrices--

Considerable emphasis has been placed on the analysis of biological materials for the presence of PCBs. Tissues are generally homogenized and ground with sodium sulfate, sand, or Florisil and are either Soxhlet extracted (Bagley et al., 1970; Curley et al., 1971; deVos, 1972; Hattula, 1974; Holden, 1971; Kuehl et al., 1980; Stalling et al., 1972) or packed into a chromatographic column and the PCBs are eluted with an appropriate solvent (Bowes and Lewis, 1974; Call et al., 1974; Donkin et al., 1977; Erney, 1974b; Ernst, 1974; Hattula, 1974; Stalling, 1971; Wardall, 1977; Hutzinger et al., 1974; Stalling et al., 1972; Sawyer, 1973; Armour and Burke, 1970). Recently, microcontinuous liquid-liquid extraction combined with steam distillation has been shown to be an effective extraction procedure for tissues (Kuehl et al., 1980).

Other tissue extraction techniques have included blending with chloroform and methanol mixtures followed by centrifugation (Sherma, 1975) and saponification of fat and animal tissue with methanolic potassium hydroxide followed by liquid-liquid extraction with hexane (Adams et al., 1979). PCBs in serum and blood samples have been extracted by dilution with methanol followed by liquid-liquid extraction with either hexane or diethylether.

Miscellaneous--

The other materials that have been analyzed for PCB content include transformer oil, silicone fluids, chlorinated benzenes, paper, packaging materials, and pigments. Generally, transformer oils, silicone fluids, and chlorinated benzenes are simply diluted with solvent prior to cleanup or direct analysis (Adams et al., 1979; ASTM, 1980a; EPA, 1981; Bellar and Lichtenberg, 1981; Klimisch and Ingebrigtson, 1980; Dow, 1980). The paper and packaging materials have required homogenization by grinding before Soxhlet extraction with hexane or acetone (Kurastune and Masuda, 1972; Giacin and Gilbert, 1973; Serum et al., 1973) or hydrolysis with refluxing alcoholic potassium hydroxide and final extraction with petroleum ether (Burke et al., 1976; Easty, 1973; Shahied et al., 1973).

In a method published by the DCMA (1980), extraction of phthalocyanine blue pigment required dissolution with sulfuric acid prior to hexane extraction to isolate incorporated PCBs. The PCBs in other pigments, such as phthalocyanine green and diarylide yellow are quantitatively extracted by high speed homogenization with methylene chloride (DCMA, 1980).

Only the extraction methods described for the colored pigments (DCMA, 1980) were developed for PCBs as nonAroclor chlorinated compounds. All other methods were used in studies that considered the environmental impacts of the commercially distributed PCBs as Aroclors.

CLEANUP

In addition to PCBs, a large number of chlorinated compounds, lipid materials, and sulfur are extracted from aqueous, oil, tissue, sludge, and sediment samples by the methods described above. Hence, it is necessary in many cases to provide an additional sample preparation step or cleanup to remove the coextractants that may act as interferences. Cleanup techniques vary considerably according to the particular sample matrix and needs for final instrumental analysis.

Review Articles

Sample extract cleanup procedures for PCB analyses have been partially reviewed previously (Holden, 1971; Fishbein, 1972; deVos, 1972; Hutzinger et al., 1974; Krull, 1977; Albro, 1979).

Standard Methods

Table 1 listed the cleanup procedures that are typically used with a number of standard methods for these materials. These cleanup procedures include liquid-liquid partition of the sample extract, saponification with alcoholic potassium hydroxide, addition of concentrated sulfuric acid, gel permeation chromatography, and oxidation of interferences in the sample matrix.

Primary Literature

Adsorption Chromatography Cleanup--

Perusal of the literature indicates that adsorption column chromatography is the most often practiced method of sample extract cleanup prior to instrumental analyses. The extent of sample cleanup required is dependent, in many cases, on the specificity of the detector used for identification and quantitation. Electron capture and halogen specific detectors (i.e., Hall electrolytic conductivity detector) require clean extracts since so many other compounds can interfere.

Chromatographic column cleanup procedures have been used extensively with adsorbents such as Florisil, silica gel, and alumina. Cleanup procedures may require the use of only one column, combinations of adsorbent materials, use of an adsorbent following liquid-liquid partition, or cleanup after matrix destruction by sulfuric acid or saponification. Proper activation of adsorbed materials and the characterization of the degree of activation is essential for effective and reproducible cleanup of sample extracts by a particular chromatography procedure (Edwards, 1974; Zitko, 1972). Reproducibility of a column method requires avoidance of overloading the column, accidental deactivation of the adsorbent during cleanup, and use of pure solvents (Edwards, 1974). Optimum cleanup and separation of PCBs from interferences require fully activated adsorbents, and large eluent volumes (Edwards, 1974; Albro and Parker, 1980). The alternative to large eluent volumes is to use only a fraction of the extract with microcolumn adsorbent procedures. A notable example is the Sep Pak marketed by Waters Associates. Several investigators have reported the application of Sep Pak for PCB cleanup as discussed below.

The most commonly used adsorbents are Florisil and silica gel at various levels of activation. Florisil has been used to remove gross interferences from sample extracts from air, water, wastewater, tissues, and dairy products as well as paper, paperboard, and paper mill effluent (AOAC Methods, 1980; Adams et al., 1979; Delfino and Easty, 1979; Easty, 1973; EPA, 1979a; EPA, 1979b; EPA, 1978; EPA, 1980; Kamops et al., 1979; Kuehl et al., 1980; Modi et al., 1976; Price and Welch, 1972; Reynolds, 1971; Reynolds, 1969; Robbins and Willhite, 1979; Rodriguez et al., 1980; Stijve et al., 1974; Swift and Settle, 1976; Tessari and Savage, 1980; Yakushiji et al., 1978; Bagley et al., 1970; Bagley and Cromartie, 1973; Bellar and Lichtenberg, 1976; Chau and Babjak, 1979). Florisil has also been used to provide additional separation of sample extracts following initial cleanup of matrices by low temperature precipitation, acetonitrile partitioning, oxidation, sulfuric acid digestion, alumina chromatography, or gel permeation chromatography (Eden, 1976; Ernst et al., 1974; Kohli et al., 1979; Mes et al., 1977a, Mes et al., 1977b; Mulhern et al., 1972; Stanovick et al., 1973; Swift and Settle, 1976; Tessari and Savage, 1980; Trotter, 1974; Uk et al., 1972; Bagley et al., 1970; Bagley and Cromartie, 1973; Copeland and Gohmann, 1982).

Seidl and Ballschmiter (1976b) investigated the recovery and efficiency of cleanup methods for the isolation of PCBs from vegetable oils. Column chromatography on Florisil, matrix destruction via saponification and sulfuric acid treatment, and liquid-liquid partition with hexane/acetonitrile or hexane/dimethylformamide were compared as cleanup techniques. The Florisil chromatographic column with hexane/methylene chloride (80:20) as the eluent and liquid-liquid partition with hexane/dimethylformamide were shown to be the methods of choice with recoveries of greater than 90%.

Silica gel or silicic acid has also been used for a large number of sample matrices including water, sediments, sludges, foodstuffs, tissues, and transformer fluids (Armour and Burke, 1970; Devinish, Harling-Bowen, 1980; Erickson and Pellizzari, 1977, 1979; Ernst, 1974; Giacin and Gilbert, 1973; MacLeod, 1979; Masumoto, 1972; Mes et al., 1976; Mes and Campbell, 1977; Nose, 1973; Ogata et al., 1980; Picer and Abel, 1978; Price and Welch, 1972; Sawyer, 1973; Stalling, 1971; Steichen et al., 1981, 1982; Balya and Farrah, 1980; Beezhold, 1973; Bellar and Lichtenberg, 1975; Coburn et al., 1977).

Many applications have utilized the excellent separation properties of silica gel to remove other halogenated interferences from PCB fractions. The separation of a number of halogenated pesticides has been accomplished by using silica gel after preliminary cleanup of gross interferences and controlling the degree of activation and size of the column or by slightly modifying the adsorbent with silver nitrate or an oxidizing agent (Erney, 1974a; Erney, 1974b; EPA, 1978; Herzel, 1971; Huckins et al., 1976; Kreiss et al., 1981; Kveseth and Brevick, 1979; Leoni, 1971; Mitzutani and Matsumoto, 1973; Musial et al., 1974; Needham et al., 1980; Public Health Services, CDC, Atlanta, 1980; Serum, 1973; Snyder and Reinert, 1971; Stratton, 1977, Swift and Settle, 1976; Trevesani, 1980; Underwood, 1979; United Kingdom, Department of Environment, 1979; Wakimoto et al., 1975; Bidleman et al., 1978).

Cleanup and separation of interferences from PCBs has been accomplished with Sep Pak miniature silica gel cartridges for transformer (Gordon et al., 1982; Steichen et al., 1981), mineral, phosphate ester, glycol base, and sulfonated mineral oils (Balya and Farrah, 1980).

Alumina has been used as an adsorbent in more recent applications for cleanup of matrices from oils, fats, and tissues (Donkin et al., 1977; Hattula, 1974; Kohli et al., 1979; Kveseth and Brevick, 1979; Ofstäd et al., 1978; Teichman et al., 1978; Wardall, 1977; Zitko, 1976) and other biological materials such as blood and human milk (Musial et al., 1972; Siyali, 1973; Tuinstra and Traag, 1979a, 1979b; Welborn et al., 1974) and from oil, water, sediments, and vegetable materials (Goerlitz and Law, 1974; Lewis et al., 1977; Tuinstra et al., 1981; United Kingdom, Department of Environment, 1979).

Dispersion of activated carbon on polyurethane foam, termed carbon foam chromatography, and use of activated charcoal have also proven to be effective means of isolating PCBs from complex matrices such as tissues and sediments (Chau and Babjak, 1979; Jensen and Sundström, 1974; Stalling et al., 1979a; Stalling et al., 1979b; Stalling et al., 1978; Stalling et al., 1975; Tiechman et al., 1978).

Gel Permeation Chromatography--

Gel permeation chromatography (GPC) has arisen as a popular cleanup procedure for complex matrices, especially samples containing macromolecular interferents such as biological materials containing high levels of lipid materials. The GPC method has been fully automated for large numbers of sample extracts. However, it is necessary to fully validate the GPC method for each different sample matrix as with other cleanup procedures.

Gel permeation chromatography has been successfully used as a cleanup for matrices of high molecular weight content and has provided a cost effective approach towards automation of large numbers of samples (Albro, 1979; Caragay and Levins, 1979; Griffitt and Craun, 1974; Haile and Lopez-Avila, 1981; Hopper and Hughes, 1976; Kohli et al., 1979; Kuehl et al., 1980a, 1980b; Rodriguez et al., 1980; Stalling, 1971, 1976; Stalling et al., 1972, 1979; Tessari, 1980). Gel permeation chromatography of tissue and vegetable material extracts followed by carbon-foam chromatography provides a cleanup that is exceptionally selective for planar aromatic hydrocarbons and the chlorinated analogs such as PCBs (Dougherty et al., 1980). Lipidex was shown to separate PCBs and other semivolatile halocarbons from water, fat, butter, and milk (Egestad et al., 1982). Elution conditions could be adjusted to separate the halocarbons from steroids and fatty acids. The authors noted that a combination of partition, molecule sieving, and aromatic adsorption was involved in the separation.

High Performance Liquid Chromatography and Thin Layer Chromatography--

High performance liquid chromatography (Aitzetmüller, 1975; Dolphin and Willmott, 1978; Rohleder, 1976) and thin-layer chromatography (Fishbein, 1971; Hattula, 1974; Koeniger, 1975) have also received limited attention as chromatographic cleanup methods. Recently, an HPLC cleanup method for determination of PCBs in oils and waste oils has been devised (Chesler et al., 1982).

Acid Cleanup--

Sulfuric acid is added as the first step of many cleanup procedures to remove gross interferences, although a number of studies found sulfuric acid cleanup alone sufficient for PCB analysis (Ahling and Jensen, 1970; Becker and Schulte, 1976; Haile and Baladi, 1977; Hattula, 1974; Mattson and Nygren, 1976; Murphy, 1972; Veierov and Aharonson, 1980; Harris and Mitchell, 1981). Losses of the mono- to trichlorobiphenyls were reported in two studies (DCMA, 1981; Lincer, 1973) which used a heated sulfuric acid cleanup. No losses were observed at room temperature (Haile and Baladi, 1977). The chemical destruction cleanup methods are extremely useful but care must be taken to ensure valid recoveries of the particular PCB isomers of interest. For example, mono-, di-, and trichlorobiphenyl isomers were not quantitatively removed from pigment matrices that were treated with concentrated sulfuric acid (DCMA, 1981; Lincer, 1973). Low recoveries were presumed to be due to sulfonation of the biphenyl ring (Lincer, 1973).

Liquid-liquid Partitioning--

Liquid-liquid partition is also used to remove large amounts of interferences from water, wastewater, milk, food products, packaging materials, silicone fluids, oil, and tissue extracts before final cleanup by a chromatography technique (EPA, 1978; Gordon et al., 1982; Leoni et al., 1973; Mulhern et al., 1972; Siyali, 1973; Swift and Settle, 1976; Tessari, 1977; Tessari and Savage, 1980; Klimisch and Ingebrigtson, 1980; Welborn et al., 1974). Large amounts of an interference in a sample extract, such as the lipid content of a tissue extract, has a pronounced effect on the efficiency of liquid-liquid partition cleanups (Albro, 1979). Validation of a cleanup procedure using spiked blanks provides much better recovery values than can be achieved for an actual sample. Therefore, it is necessary to spike actual sample extracts to fully characterize the limitations of this type of cleanup step. Seidl and Ballschmiter (1976b) have demonstrated PCB recoveries of greater than 90% for cleanup of vegetable oil extracts by liquid-liquid partition with hexane and dimethylformamide.

Saponification--

Saponification of the sample matrix has been discussed as a method for extracting PCBs from certain materials. Saponification may also be considered a cleanup procedure (Lincer, 1973; Tatsukawa and Wakimoto, 1972; Trotter, 1974). Saponification of sample matrices with ethanolic potassium hydroxide has been accomplished without chemical change to the PCBs present (Young and Burke, 1972).

Miscellaneous--

Other cleanup procedures that have been shown to be effective but have limited use are low temperature precipitation of lipids from tissues and human milk samples prior to solvent extraction or liquid-liquid partitioning (Mes et al., 1977a, 1977b; Mes and Campbell, 1976). Oxidation of interfering chloronaphthalenes and chlorinated pesticides such as DDT and DDE with chromium trioxide or chromic acid has been shown to be effective when used in conjunction with a final chromatographic cleanup (Holmes and Waller, 1972; Mulhern et al., 1972; Underwood et al., 1979). However, Szelewski et al. (1979) have questioned the reliability of the chromium trioxide oxidation of interferences in sample extracts. Fish extracts, spiked with Aroclor 1016, 1221, and 1254, were treated with the chromium trioxide oxidation technique. Recoveries of Aroclor 1016 from this oxidation step ranged from 30 to 90% for eight replicates, while Aroclor 1254 recoveries ranged from 40 to 80% for eight replicates. Aroclor 1221 was reported to have 0% recovery from this oxidation step for six replicate samples. Szelewski et al. (1979) theorized that PCBs in the extracts were lost by oxidation, by volatilization due to the highly exothermic nature of the oxidative process, or a combination of the two. Steam distillation of water, sediments, and tissues provides relatively clean extracts that require little or no additional cleanup (Veith and Kiwus, 1977; Dougherty et al., 1980). Interference from elemental sulfur is a serious problem, especially for electron capture detector methods of analysis. The sulfur interference in water, wastewater, sewage sludges and sediments can be effectively removed by precipitation of sulfur with mercury (Bellar and Lichtenberg, 1976; Goerlitz and Law, 1974; Rodriguez et al., 1980) or by converting sulfur to thiosulfate by addition of tetrabutylammonium sulfate (Jensen et al., 1977).

Recovery Measurement

Regardless of the cleanup procedure required for PCB analysis from a particular sample, it is of utmost importance to document recovery of PCBs from the method. Routine quality assurance governs that the recovery be determined for each different sample matrix encountered. Also, recovery of the PCBs should be determined each time a given parameter of an established cleanup procedure is changed. For example, different batches of an adsorbent may differ greatly with respect to activation. Cleanup steps should be monitored with spiked samples to support overall quality of the data. In some instances, a visible marker such as azulene can be used as a real time monitor to determine the performance of column chromatography methods (Nowicki, 1981).

DETERMINATION

Thin-Layer Chromatography

In addition to its use as a cleanup technique, thin-layer chromatography (TLC) has been used extensively as a determination technique. TLC was used early (latter 1960s, early 1970s) because HPLC was not readily available and the GC techniques were not well-developed. Most of the early TLC reports were normal phase (silica gel) and included elaborate cleanup steps to remove interferents (e.g., oxidation of DDE to a benzophenone derivative).

In the mid-1970s when packed column gas-liquid chromatography/electron capture detection (PGC/ECD) became the method of choice, emphasis on TLC methods dwindled. Several articles have been published which take advantage of modern TLC techniques: high performance TLC, two-dimensional TLC, reverse phase TLC, and new detection methods.

TLC has been shown to be an effective technique for determination of (Aroclor) PCBs in a wide variety of matrices. The advantages included its ease of use and the simplicity of the apparatus. The disadvantages include lack of resolution, moderate sensitivity, and specificity.

Review Articles--

TLC analysis of PCBs was reviewed by Fishbein (1972).

Standard Methods--

TLC is included as an alternate technique for "semiquantitation" analysis of PCBs in human adipose tissue in EPA manuals (Watts, 1980; Sherma, 1981). It is also included in the Association of Official Analytical Chemists methods for confirmation of identity (AOAC, 1980).

TLC is mentioned by the Food and Drug Administration (1977) as a technique which they feel may also be useful in dealing with particular resin combinations.

Primary Literature--

Since the publication of a TLC method for PCBs by Mulhern (1968) and Mulhern et al. (1971), several researchers have used a similar method for analysis of PCBs in food (Stijve and Cardinale, 1974), animal feeds (Westoo and Noren, 1970), food packaging (Zimmerli et al.), bald eagles (Bagley et al., 1973), Aroclor mixtures (Willis and Addison, 1972), animal tissue (Collins et al., 1972; Koeniger et al., 1975; Bush and Lo, 1973; Hattula, 1974; Mes et al., 1977), human adipose tissue (Price and Welch, 1972; Lucas et al., 1980), and human milk (Savage et al., 1973a, 1973b; Mes and Davies, 1979).

Many of these researchers employed TLC in conjunction with other techniques such as GC/ECD. Often, TLC was used as a confirmation technique.

Several publications have reported developments claimed to improve the technique. Circular TLC reportedly improves sensitivity by an order of magnitude with a PCB limit of detection of about 0.05 µg (Koch, 1979). Fused glass TLC has been reported as yielding longer plate life (Okamura et al., 1973). Reverse phase TLC has been reported to yield better separation of PCBs from interferences (deVos and Peet, 1971; deVos, 1972; Stalling and Huckins, 1973; Brinkman et al., 1976a). An impregnated silica gel plate has been reported (Bergman et al., 1976) which improves selectivity apparently on the basis of ion-pairing. The use of surfactant micellar solutions as the mobile phase is certainly novel and reportedly has potential for separation of chlorinated aromatics, including decachlorobiphenyl (Armstrong and Terrill, 1979). Improvements in detection have included an $AgNO_3$ spray followed by UV irradiation (deVos and Peet, 1971; deVos, 1972; Kawabata, 1974) and fluorescence (Kan et al., 1973; Ueta et al., 1979). A two-dimensional TLC method was developed which barely separated the DDT analogs from PCBs (Fehringer and Westfall, 1971).

This last reference points to one of the major problems with TLC determination of PCBs. Many common interferences (e.g., DDE in biological tissues) have similar elution characteristics and are not easily resolved. One common technique for removal of DDE prior to TLC is oxidation of the DDE to dichlorobenzophenone with chromium trioxide or other oxidant (Biros et al., 1972; Sherma, 1981; Watts, 1980; Collins et al., 1972).

Two studies (Bush et al., 1971; Collins et al., 1972) compared TLC and GC/ECD. In both studies the PCB values obtained were generally comparable, although in the study by Bush et al., the TLC results were generally lower than GC/ECD.

Lucas et al. (1980) reported a statistical analysis of semiquantitative determinations of PCBs in human adipose tissue generated by the EPA's National Human Monitoring Program during FY 1972 to 1976. Results were reported only as ranges (not determined, < 1, 1 to 3, and > 3 ppm) for 5,259 samples. The EPA TLC technique (Watts, 1980; Sherma, 1981) was used in this study through November 1974 and a GC/ECD technique involving a single PCB peak quantitation was used thereafter. A total of 3,802 TLC results and 1,457 PGC/ECD results were compared and not found significantly different.

High Performance Liquid Chromatography

High performance liquid chromatography (HPLC), with ultraviolet and other detectors, has been reported in the characterization of commercial PCBs as a cleanup technique and as an analytical technique. Despite its general applicability in analytical chemistry, HPLC has not been as popular as gas chromatography (GC) for PCB analysis. The major reason is that GC detectors, especially those selective toward halogens, exhibit much lower limits of detection.

Since HPLC is basically an instrumental version of the column chromatographic cleanup techniques, described above, it is applicable both as a cleanup and a determination technique. Some researchers have exploited this and combined cleanup and determination into one step with HPLC (Hanai and Walton, 1977; Van Vliet et al., 1979).

Review Articles--

Krull (1977) mentioned HPLC in a review of PCB analysis. Lawrence and Tuiton (1978) reviewed the HPLC data on pesticides, including PCBs in their tabulation.

Standard Methods--

No standard methods utilize HPLC.

Primary Literature--

Several authors (Brinkman et al., 1976a, 1976b; Veith and Austin, 1976; Albro and Parker, 1979; Brinkman and deVries, 1979) have used HPLC in characterization of commercial PCB products or establishing the chemical behavior of PCBs.

HPLC has been used as a cleanup technique prior to gas chromatographic determination (Aitzenmüller, 1975; Dark and Crossman, 1973; Rohleder et al., 1976; Krupcik et al., 1977; Dolphin and Willmott, 1978). More recently it has been used on a preparative scale to clean up waste and transformer oils prior to CGC/ECD determination (Anonymous, 1982; Chesler et al., 1981). In the course of these investigations, the researchers noted that the CGC/ECD limit of detection was about 100 times lower than the HPLC/UV limit of detection.

As HPLC became increasingly popular in the early 1970s, Eisenbeiss and Sieper (1973) performed preliminary investigations of the use of HPLC for pesticide (and PCB) analysis. They concluded that HPLC can be regarded as an alternative or supplementary method to conventional methods such as gas chromatography.

Hanai and Walton (1977) developed an HPLC/UV method for determining PCBs in water. No LOD was determined, but good recoveries were obtained for 250-µg/liter Aroclor 1232 spiked into distilled water. The water was pumped directly through the HPLC system and the PCBs subsequently eluted by gradient elution. A similar application (Van Vliet et al., 1979) used an HPLC precolumn to concentrate PCBs from water and then elute them onto the analytical column for separation and determination.

Belliardo et al. (1979) developed an HPLC/UV procedure for PCBs in oil and compared it with a PGC/ECD method. The HPLC method was judged suitable to approximate, but not quantitate, the PCB content.

Seidl and Ballschmiter (1979) used HPLC/UV to detect biphenyl after dehydrochlorination of PCBs.

Electron capture detection of HPLC effluents has been described (Willmott and Dolphin, 1974) for the analysis of PCBs. The LOD of HPLC/ECD is reported to be about 10 times higher than for GC/ECD (Brinkman et al., 1978). Stalling et al. (1980) gave a preliminary description of an HPLC/MS (presumably the chemical ionization MS mode) system for rapid screening for PCBs.

Gas Chromatography

Gas chromatography (GC), in combination with various detectors, has been by far the most popular and useful analytical procedure for PCBs. In recent years, capillary column GC (CGC) has been used increasingly, although most investigators still use packed column GC (PGC). The popularity of GC lies in its resolution and speed (most PGC analyses take less than 30 min) and the sensitivity (ECD), selectivity (ECD, HECD), and specificity (electron impact mass spectrometry) of the available detectors.

Separation--

Packed column GC (PGC)--Over 215 references were abstracted which used PGC as the analytical separation technique. The vast majority of these used PGC in a routine manner with a common liquid phase. The quality of the chromatography (resolution and tailing) was generally adequate for low resolution separation of Aroclor-derived samples into a "fingerprint" for identification or quantitation. Since the Aroclor mixtures are too complex for resolution, little or no emphasis was placed on improving resolution by PGC.

The most common PGC detector has been ECD. ECD has historically required isothermal GC operation (not so with modern instruments). Figures 1 and 2 present some PGC/ECD chromatograms (Mullin and Filkins, 1981).

Review articles--By 1971 sufficient work in PCB analysis by PGC had been completed to merit a review (Reynolds, 1971). This was followed by several other reviews (Fishbein, 1972; Hutzinger et al., 1974; Fuller et al., 1976; Krull, 1977; Margeson, 1977; and CMA, 1981). One review by Sherma (1975) was devoted to PGC analysis of PCBs and related chlorinated aromatic pollutants.

Standard methods--PGC is the recommended analytical separation method in all but one of the 11 standard methods listed in Table 1.

Primary literature--Since over 215 citations on the use of PGC in the analysis for PCBs have been abstracted, a complete discussion of the primary literature would be a formidable task. Most of these citations used PGC in a routine manner and included little or no discussion as to why a liquid phase or GC condition was chosen (if they were even mentioned). Several articles are worth noting.

Albro et al. (1977) evaluated 13 packed columns ranging in polarity from Apiezon L to OV-225. The number of observed theoretical plates ranged from 491 to 3,833. None of the columns could successfully resolve all PCBs. In the best case, it was calculated that of the 21,945 theoretically possible pairs of PCB congeners, 465 would be indistinguishable using the best column tested. The researchers discussed the use of multiple columns for resolving indistinguishable pairs and concluded that five columns were necessary to resolve all isomers. Thus, using this scheme, each sample would have to be analyzed once on each of five PGC columns to resolve all congeners.

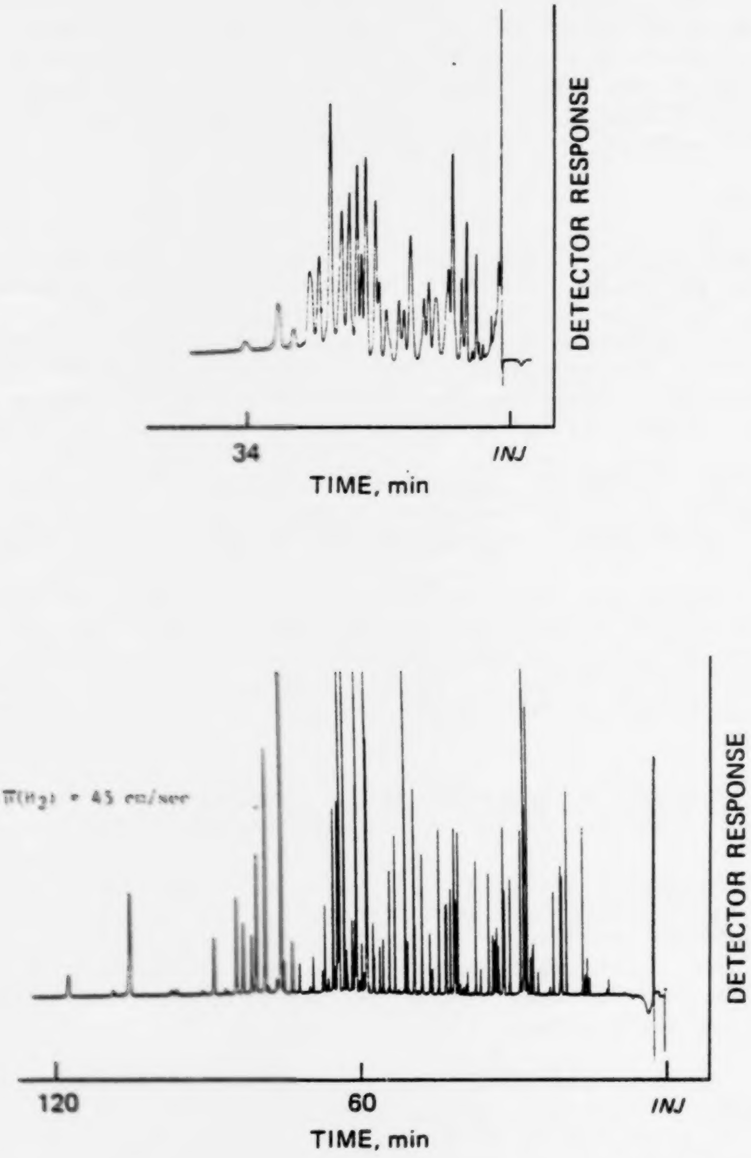


Figure 1. Comparison of packed column gas-liquid chromatography (top) and capillary column gas-liquid chromatography (bottom) with Aroclor 1242 and 1260 standards (Mullin and Filkins, 1981).

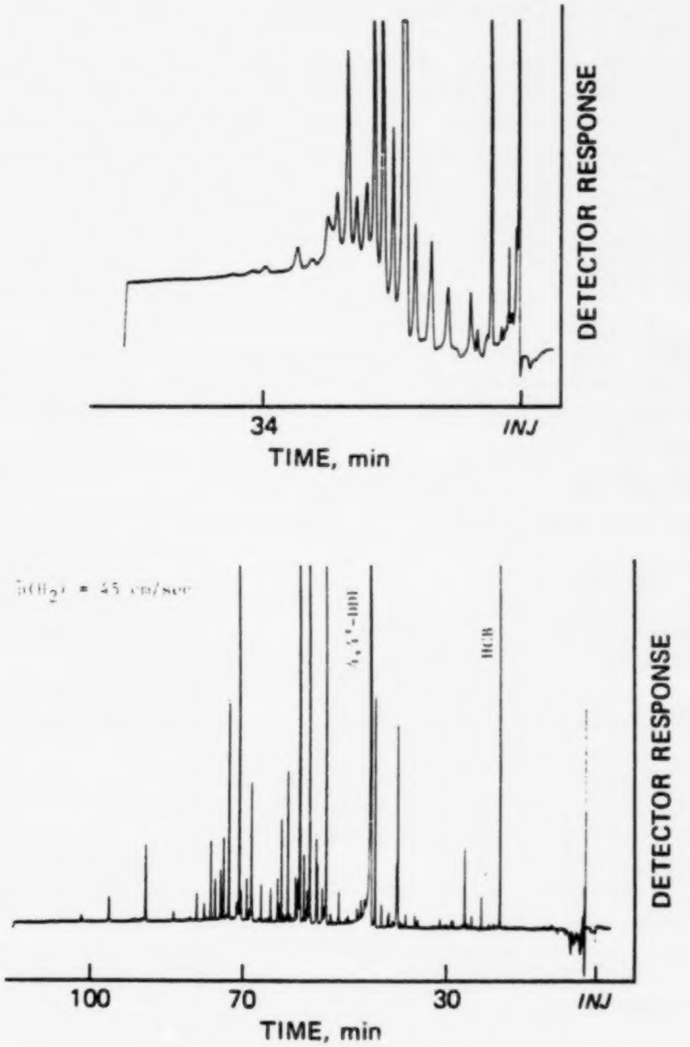


Figure 2. Comparison of packed column gas-liquid chromatography (top) and capillary column gas-liquid chromatography (bottom) with a milk extract (Mullin and Filkins, 1981).

Albro and Parker (1979) applied this technique to the identification of the components in Aroclor 1016 and 1242. The identity of 44 congeners was reported.

A report by Jensen and Sundström (1974) presents what may be the highest resolution PGC chromatogram of PCBs. Even though it was operated isothermally, this 5.2-m Apiezon L column resolved 59 peaks in a Chlophen mixture.

Capillary column gas chromatography--CGC has not been nearly so popular as PGC, although 42 citations have been abstracted. In recent years the quality of the CGC separations reported have been truly impressive. Despite these advances, no CGC method reported or predicted will separate all 209 PCB congeners. As an example of the overlap problem, Pellizzari (1982a) reported CGC/ECD and CGC/NCIMS identification of PCB congeners in an Aroclor 1016/1254/1260 mixture. Of the 103 peaks listed, 73 were identified, but only 43 corresponded to a single congener. The others were possibly two (19 peaks), three (9 peaks), four (1 peak), or even six (1 peak) co-eluting congeners.

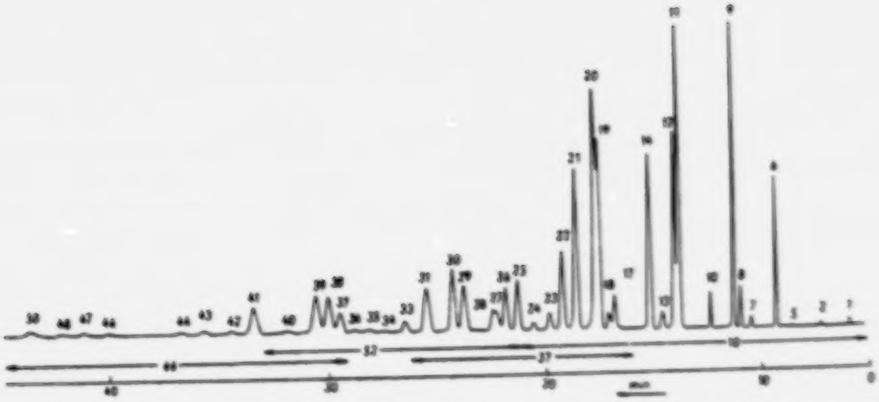
In addition to the problem of congener separation, interferences may coelute. EIMS can readily discriminate against non-PCBs; however, co-eluting major components may affect the mass spectral response of PCBs.

Review articles--CGC was briefly cited (five references) in one review (Sherma, 1975). An Aroclor CGC/ECD chromatogram was included in a CGC monograph (Jennings, 1978) as an application of CGC.

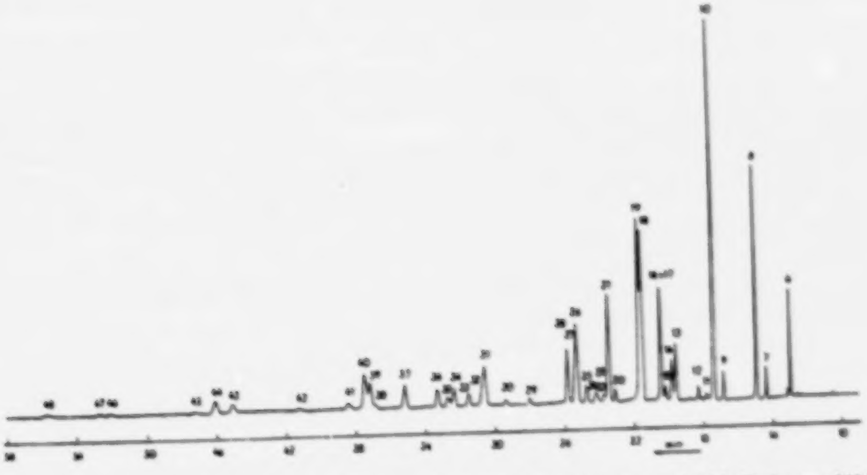
Standard methods--One of the 11 standard methods in Table 1 recommends CGC, specifically a support coated open tubular (SCOT) column coated with FFAP (free fatty acid phase) for analysis of PCBs in capacitor Askarels. EPA Method 625 (EPA, 1979b) recommends PGC or if desired, capillary or SCOT columns may be used. Capillary gas chromatography is also allowed, if desired, for the analysis of PCBs in transformer fluids or waste oils (EPA, 1981).

Primary literature--CGC was utilized in 43 articles abstracted for this review. The level of detail and column specifications span a wide range. Sissons and Welti (1971) published an early article which characterized many of the PCB isomers in Aroclor 1254. Using an Apiezon L packed column, 23 peaks were resolved, while the same phase on a SCOT column (24,000 to 27,000 plates) separated 65 peaks. The next year, Webb and McCall (1972) performed similar experiments using an SE-30 SCOT column. Although the resolution was poor by today's standards, Biros et al. (1970) used CGC/EIMS to determine PCBs in human adipose even earlier.

Krupcik et al. (1971) evaluated metal WCOT columns coated with Apiezon L or OV-101 and found them unsuitable. However, OV-101 on a glass WCOT column gave good results. An example of the separations obtained by CGC using liquid phases of different polarity is shown in Figure 3 (Krupcik et al., 1977). The quality of the chromatography is less than optimal because the GC was operated isothermally. Krupcik et al. (1982) have also reported on the optimization of experimental conditions for the analysis of complex mixtures by capillary gas chromatography. The optimization procedure for complex materials was demonstrated with Aroclor 1242. Forty PCBs were separated



Separation of a PCB mixture by GLC on a glass capillary column coated with OV-101 at 200 °C (column E).



Separation of PCB mixture by GLC on a glass capillary column coated with Carbowax 20M at 200 °C (column F).

Figure 3. Comparison of PCB resolution on different columns (Krupcik et al., 1977).

at 170°C using a 40.0 m Carbowax 20M glass capillary column connected to a 75.6 m Apiezon L glass capillary column.

Using a 50-m Dexsil 410 glass capillary Albro et al. (1981) have achieved 175,000 effective theoretical plates for 2,3,5,2',3',5'-hexachlorobiphenyl. Resolution of Aroclor 1260, which required an isothermal chromatogram of 5 h, generated 110 peaks, of which only 4 were unidentified. Even at this resolution, the Dexsil 410 did not resolve all congener pairs. Less efficient columns coated with Silar 5 C, Apiezon L, and OV-25 were used to provide different separations which resolved the congener pairs not previously resolved.

Although no column performance parameters were given, Mullin and co-workers have achieved impressive resolution by temperature-programmed CGC/ECD on C-87 columns (Mullin and Filkins, 1981; Mullin et al., 1981) and SE-54 columns (Safe et al., 1982).

Pellizzari et al. (1981) have compared a number of capillaries (capillary material, pretreatment, and liquid phase). Apiezon L was judged to be the best of the liquid phases tested (SE-54, C-87, SP-2100, and Apiezon L), for PCB analysis, based on resolution, separation number, and HEETP. Two examples of this column's performance are shown in Figures 4 and 5. This conclusion supports that of several other investigators who have used and recommend Apiezon L (Sissons and Welti, 1971; Albro et al., 1977; Stalling et al., 1978; Albro et al., 1981; Jensen and Sundström, 1974; Nakamuna and Kashimato, 1977; United Kingdom Department of the Environment, 1979) or similar hydrocarbon phases for PCB analysis (Mullin and Filkins, 1981).

Tuinstra and coworkers (Tuinstra and Traag, 1979a, 1979b; Tuinstra et al., 1980; Tuinstra et al., 1981) have explored the automation of CGC/ECD analysis with autoinjection onto a splitless injector. This approach, although not thoroughly presented in Tuinstra (no mention of sample throughput or automation of data recording and reduction is mentioned), should be pursued by laboratories facing large sample loads.

Recently, bonded liquid phases have been made available on capillary GC columns. These exhibit low bleed and background and have long lifetimes. Figure 6 presents a CGC/EIMS chromatogram of a PCB standard on a DB-5 column.

It is interesting to note that J&W Scientific, Analabs, and Supelco present CGC/ECD chromatograms of Aroclor mixture in their catalogs. This indicates that CGC is commercially available and that the capillary manufacturers consider their PCB separations good enough to advertise.

Comparison of PGC and CGC--The relative merits of PGC and CGC are well-known and apply to the separation of PCBs. CGC provides better resolution, retention time precision, and higher qualitative reliability. PGC yields a simple chromatogram (less data reduction), permits higher sample loading (and therefore possibly lower LOQs), and is generally considered easier to use. Historically, PGC quantitation has been more precise, although it has not been established how much of the imprecision attributed to CGC has been due to poor technique on the part of the analyst.

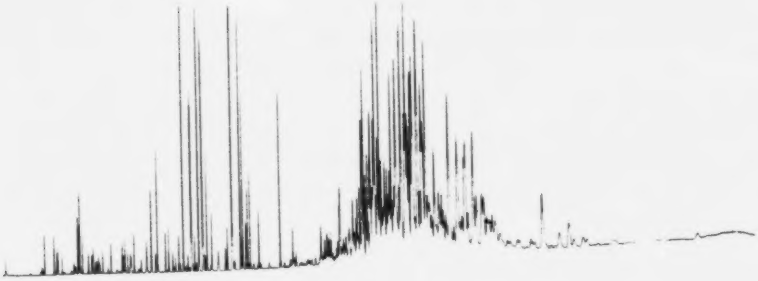


Figure 4. Electron capture detection of Aroclors 1242, 1260, and 5460 (400 pg each) chromatographed on an Apiezon L (WCOT) silanized Pyrex glass capillary, 0.20 mm i.d. x 50 m in length. The carrier was 53 cm/s; capillary was temperature-programmed from 150 to 390°C at 1°C/min (Pellizzari et al., 1981).

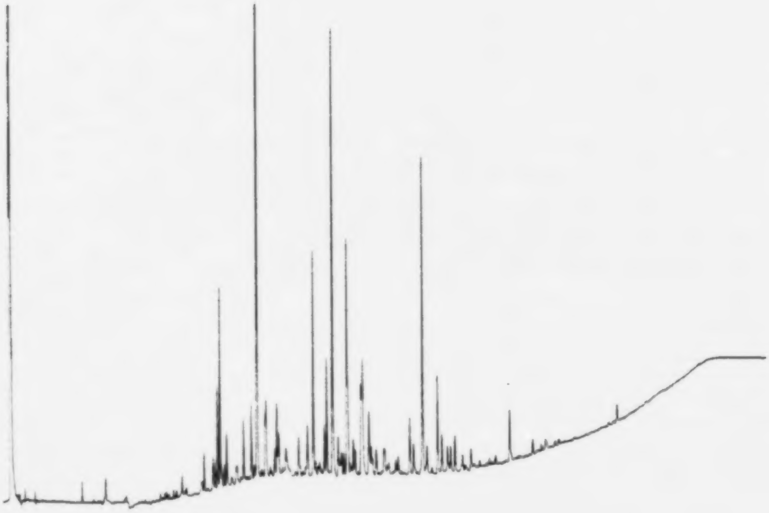


Figure 5. Electron capture detection of PCB in an extract of yellow perch. See Figure 4 for chromatographic conditions (Pellizzari et al., 1981).

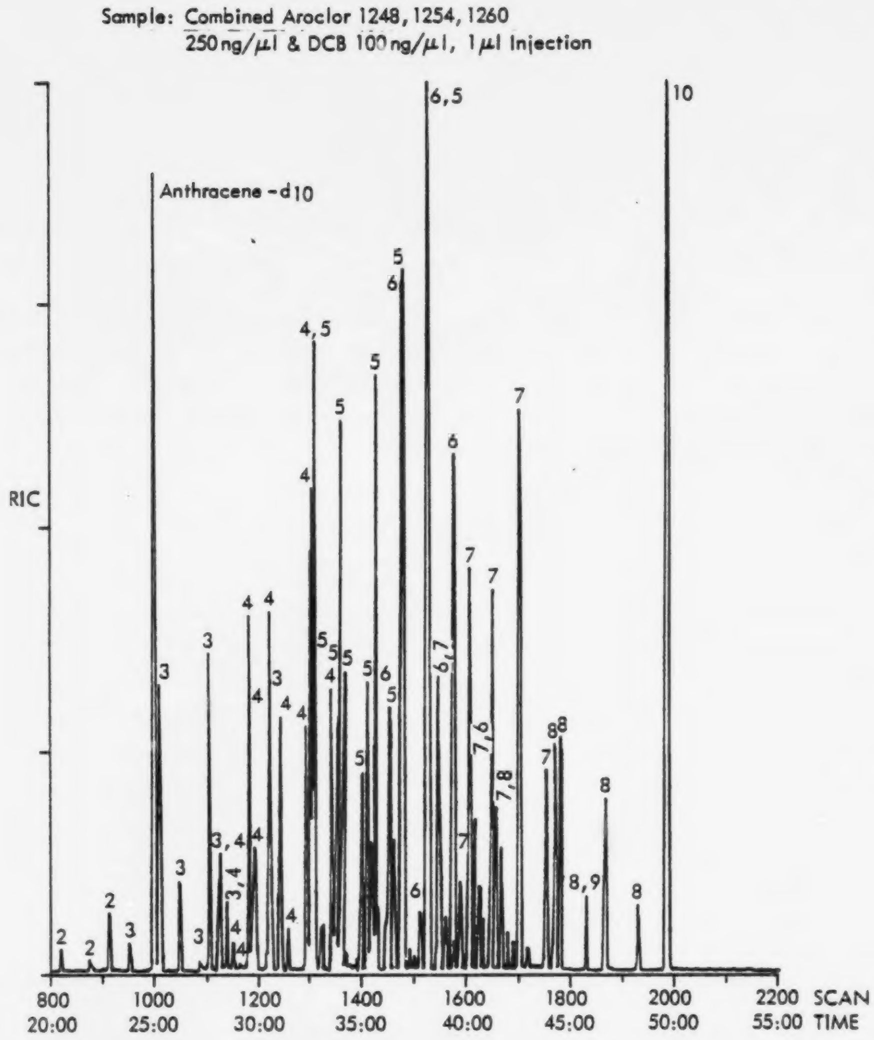


Figure 6. Scanning capillary column gas-liquid chromatography/mass spectrometry analysis of a mixed Aroclor standard used to establish retention windows for the CGC/MS-selected ion monitoring analysis of PCBs.

Instrumental parameters: column, 15-m, fused silica, DB-5; column temperature, 80°C for 2 min, 8°C/min to 300°C; helium carrier at 2.5 psi; J&W on column injector. (J. S. Stanley and C. L. Haile, Midwest Research Institute, personal communication, 1982).

Figures 1 and 2 (Mullin and Filkins, 1981) present graphic comparisons of PGC and CGC results for PCBs. Similar results have been presented by Onsuka and Comba (1978).

Detectors--

GC detectors are classified as either universal or selective. The ECD and HECD are highly selective toward halogenated compounds. This selectivity, coupled with its extreme sensitivity, has made ECD very popular for analysis of trace levels (residues) of pesticides and PCBs and has, in fact, had a significant role in regulatory actions on these classes of compounds. FID is the most common GC detector and is a universal detector, giving similar responses for most organic compounds. Thus, FID would be unsuitable for detection of PCBs in a complex matrix.

Mass spectrometry and Fourier transform infrared spectrometry (FTIR) are in essence both universal and selective GC detectors. By focusing on a spectral property characteristic of a compound or class of compounds, these detectors can be quite specific. However, by using the full spectral range, nearly any compound eluting from the GC will be detected. Due to the much higher information content of mass and infrared spectra, identifications by GC/MS or GC/FTIR are generally made with greater certainty than by other detectors.

The analysis of PCBs generally requires selectivity and sensitivity. Usually, even after cleanup, PCBs are a minor component of the sample, mixed in with other halocarbons (e.g., DDE), hydrocarbons, lipids, etc. Thus, the detector must selectively detect PCBs in the presence of other compounds present at orders of magnitude higher concentration. Furthermore, the levels typically observed in food, biota, tissue, soil, and other matrices of interest are in the parts per billion range. These levels strain the capabilities of even the most sensitive detection device such as ECD, resulting in a large number of "not detected" values in many reports.

The choice of detector often depends upon the level of analytes. Low concentrations demand a detector capable of detecting low amounts (high sensitivity). Figure 7 presents the typical range and detection limits for most of the GC detectors used in analysis for PCBs. The detection limit of the HECD is 10^{-11} g with a linear range up to about 10^{-2} g, as measured for lindane (Anderson and Hall, 1980). As can be seen, ECD exhibits the lowest limit of detection (LOD).

The reported LOD for PCBs in a variety of matrices are listed in Table 2. Comparison of the reported LODs is difficult because no standard definition of LOD was used. Glaser et al. (1981) followed a rigorous definition and experimentally determined the LOD with a fair degree of confidence, while other investigators clearly guessed at the LOD based on this work. The issue is further clouded by inconsistency in discussing the LOD with respect to the instrumental determination versus the entire procedure. Some LODs are reported for standard solutions, while others take into account the interferences in the matrix which often raise the LOD considerably.

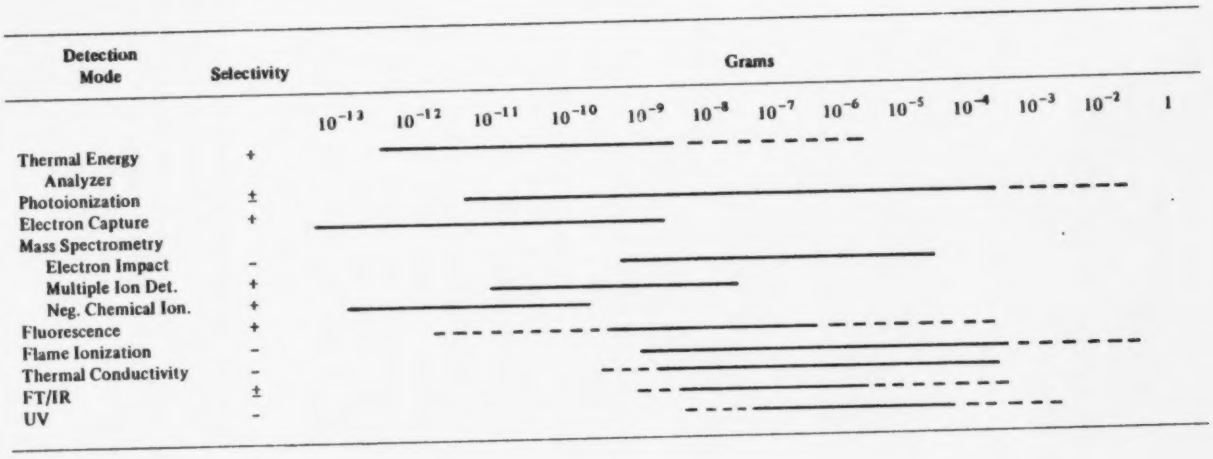


Figure 7. Detection limits/dynamic range for several instrumental methods (Pellizzari, 1981).

TABLE 2. REPORTED LIMITS OF DETECTION FOR PCBs

Instrument	Reported LOD	Converted LOD[a] (μg/g or ppm)	Substance	Matrix	Reference
GC/ECD	0.065 μg/ℓ	0.000065	Aroclor 1242	Dist. water	Glaser et al., 1981
	0.5 ppb	0.0005	Aroclors	River water	Kuehl et al., 1980
	6.5 ppb	0.0065	Aroclors	Pure solution	Teichman et al., 1978
	50 ppb	0.05	Aroclors	Milk	Tessari and Savage, 1980
	1-0.1 ppb/isomer	0.001-0.0001	Isomers	Vegetable	Tuinstra et al., 1981
	0.5 ppm	0.5	Aroclors	Transformer fluid	Kirshen, 1981
	1 ppm	1.0	Total PCB	Oil	Chesler et al., 1981
	0.5 ppm	0.5	Total PCB	Oils	Balya and Farrah, 1980
	0.6 μg/ℓ	0.0006	Perchlorinated	Ground water	Stratton et al., 1979
	1 ng/m^3	NA[b]	Perchlorinated	Air	Stratton et al., 1978
	0.1 ng/m^3	NA[b]	Theoretical per isomer	Air	Lewis et al., 1977
	3 μg/ℓ	0.003	Aroclor 1260	Blood serum	Kreiss et al., 1981
	1 ppm	1 ppm	10 homologs	Pigments	DCMA, 1980
GC/HECD	1 mg/kg	1.0	Aroclors	Oil	EPA, 1981
GC/EIMS	30 μg/ℓ	0.030	Aroclor 1221	Dist. water	Glaser et al., 1981
	36 μg/ℓ	0.036	Aroclor 1254	Dist. water	Glaser et al., 1981
	0.01-0.2 μg/ℓ	0.01-0.2	Single isomer	Industiral sample extract	Tindall and Winninger, 1980
	5 ppm	5	Single isomer	Chlorinated hydrocarbons	Collard and Irwin, 1982
HREIMS	10 ppb	0.01	Aroclors	Biological extracts	Safe et al., 1975
GC/NCIMS	None				

(continued)

TABLE 2 (continued)

Instrument	Reported LOD	Converted LOD[a] (μg/g or ppm)	Substance	Matrix	Reference
Dir. Probe NCIMS	~ 1 ppb	0.001	NS[c]	Biological extracts	Dougherty et al., 1980
TLC	0.5 ppm	0.5	Aroclor	Adipose	Bush and Lo, 1973
	< 0.04 ppm	< 0.04	Aroclor	Milk	Savage, 1973
	0.1 μg	-	Aroclor	Animal tissue	deVos and Peet, 1971
	0.05 μg	-	Aroclor	NS	Koch, 1979
	0.2 μg	-	Aroclor	Animal tissue	Mulhern et al., 1971
	1 μg	-	Aroclor	NS	Ismail and Bonner, 1974

[a] Converted to common units of micrograms per gram (parts per million) assuming 1 ml = 1 g density.

[b] NA = not applicable.

[c] NS = not specified.

Reviews Articles--

Every review article abstracted covered the subject of ECD detection of GC effluents (Riseborough, 1971; Reynolds, 1971; Fishbein, 1972; Linear, 1973; Hutzinger et al, 1974; Sherma, 1975; Fuller et al., 1976; Margeson, 1977; Krull, 1977; Safe, 1976). Fishbein (1972), Sherma (1975), and Hutzinger et al. (1974) all reviewed the use of electrolytic conductivity detectors for PCB determination. Safe (1975) and Hutzinger et al. (1974) discussed the use of flame ionization detection (FID), mostly with respect to calibration of ECD or establishing ECD response factors. Hutzinger et al. (1974) did mention that for the mono- and dichlorobiphenyls FID and ECD sensitivities are comparable.

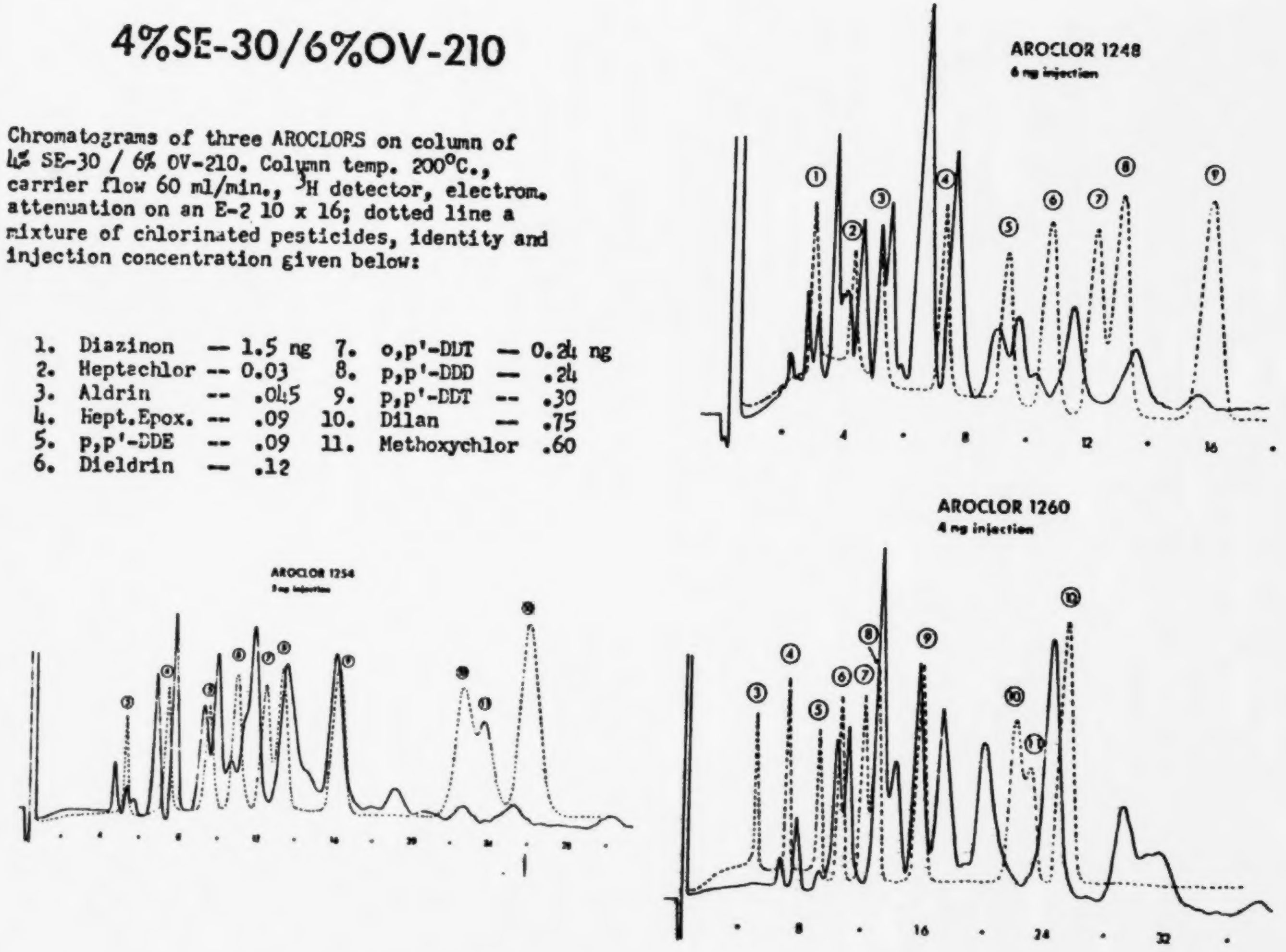
Standard Methods--

As noted in Table 1, most of the standard methods specify ECD as either the detector or one of the options. FID is the detector prescribed in the American Society for Testing and Materials (1980a) procedure for determining PCBs in capacitor Askarels. In this case, the matrix is well-characterized and generally contains no other compounds in the PCB retention window. HECD is permitted as an alternate detector in three procedures (EPA, 1978; EPA, 1981; FDA, 1977).

Electron capture detection--Based on literature citations and number of samples processed, the electron capture detector (ECD) has been the most common detector for GC analysis of PCBs. ECD is extremely sensitive for PCBs. It does, however, detect many nonPCB compounds (halogenated pesticides, PCNs, chloroaromatics, phthalate and adipate esters, and other compounds) which may be differentiated from PCBs only on the basis of retention time. Figure 8 illustrates the potential interferences from chlorinated pesticides.

A major disadvantage of ECD is the range of response factors (Tables 3 and 4) which different PCB congeners exhibit. This seriously inhibits reliable quantitation. The opposite trends in the two tables presumably result from differences in the equations used (i.e., whether the PCB response is in the denominator or numerator). The earlier PGC/ECD work (Table 3) has a range of about 1,400, while the later CGC/ECD work (Table 4) has a range of only about 120. This may be a function of the differences in detector design and GC column throughput. In addition, the CGC is temperature-programmed, while PGC data were presumably obtained isothermally. Despite these differences, both tables clearly illustrate that, even within a homolog, the % RSD is very large and would result in poor accuracy if quantitation involves extrapolation from one isomer to another. A recent report of the ECD relative response factors for all 12 octachlorobiphenyls showed a range from 0.007 to 2.644 with a RSD of 35% (Mullin et al., 1981). This also illustrates the problem of PCB quantitation by ECD. This subject is treated in more detail in the Quantitation section.

Over 175 references were abstracted in which ECD was used as a GC detector. Any novel aspects of the articles dealt with qualitative or quantitative aspects of ECD and will be treated in the appropriate subsections below.



4%SE-30/6%OV-210

Chromatograms of three AROCLORS on column of 4% SE-30 / 6% OV-210. Column temp. 200°C., carrier flow 60 ml/min., ^{3}H detector, electrom. attenuation on an E-2 10 x 16; dotted line a mixture of chlorinated pesticides, identity and injection concentration given below:

1. Diazinon — 1.5 ng
2. Heptachlor -- 0.03
3. Aldrin -- .045
4. Hept.Epox. -- .09
5. p,p'-DDE -- .09
6. Dieldrin — .12
7. o,p'-DDT — 0.24 ng
8. p,p'-DDD — .24
9. p,p'-DDT -- .30
10. Dilan — .75
11. Methoxychlor .60

Figure 8. Packed column gas-liquid chromatography/electron capture detector chromatograms illustrating potential interferences between pesticides and PCBs (Watts, 1980).

TABLE 3. RELATIVE MOLAR RESPONSES OF ELECTRON CAPTURE AND FLAME IONIZATION DETECTORS TO SOME CHLOROBIPHENYLS[a]

Chlorobiphenyl	Relative molar response	
	Electron capture	Flame ionization
2-	1.00	1.00
3-	0.20	0.92
4-	1.10	0.87
2,2'-di	5.16	0.99
2,4-di	17.7	0.86
2,6-di	32.0	0.91
3,3'-di	6.10	0.94
3,4-di	15.2	0.86
4,4'-di	5.97	0.81
2,4,4'-tri	135	0.78
2,2',4,4'-tetra	106	0.87
2,2',6,6'-tetra	20.6	0.90
3,3',4,4'-tetra	396	0.87
3,3',5,5'-tetra	320	0.85
2,3,4,5-tetra	367	0.87
2,3,5,6-tetra	259	0.71
2,2',4,4',6,6'-hexa	347	
3,3',4,4',5,5'-hexa	726	
2,2',3,3',4,4',6,6-octa	1,180	
2,2',3,3',5,5',6,6'-octa	1,150	
deca	1,410	
N	21	16
Mean	310	0.88
SD	438	0.07
RSD (%)	140	8.3

[a] Taken from Hutzinger et al., 1974, and Safe, 1975.

TABLE 4. COMPARISON OF RELATIVE RESPONSE FACTORS BETWEEN (GC)^2-ECD, GC-EIMS (MOLECULAR ION) AND (GC)^2-NICIMS (*m*/*z* 35) FOR HOMOLOGOUS SERIES OF PCBs*

Homolog series	(GC)^2-ECD[a]			(GC)^2-NICIMS[a]			GC-EIMS[b]		
	Range[d]	Mean ± S.D. (% RSD)	N[c]	Range[d]	Mean ± S.D. (% RSD)	N	Range[e]	Mean ± S.D. (% RSD)	N
1C1(3)	15.089-39.342	29.589 ± 12.78 (43)	3	0.456-1.787	0.924 ± 0.75 (81)	3	1.000-1.090	1.050 ± 0.04 (3.8)	3
2C1(12)	0.425-10.641	4.271 ± 3.83 (90)	9	2.881-21.199	8.343 ± 6.17 (74)	8	1.000-2.062	1.736 ± 0.30 (17)	10
3C1(24)	0.328-2.136	1.193 ± 0.68 (58)	9	0.721-10.901	2.921 ± 3.64 (125)	7	1.000-1.627	1.400 ± 0.24 (17)	9
4C1(42)	0.385-2.229	1.074 ± 0.41 (38)	31	0.102-4.267	2.058 ± 1.02 (50)	16	1.000-2.146	1.549 ± 0.33 (21)	11
5C1(46)	0.462-8.481	1.266 ± 1.29 (102)	35	0.465-1.216	0.805 ± 0.27 (33)	12	1.000-1.013	1.004 ± 0.01 (0.7)	3
6C1(42)	0.391-1.912	0.973 ± 0.335 (35)	37	0.369-1.440	0.817 ± 0.29 (36)	16	1.000-1.321	1.153 ± 0.11 (9.6)	7
7C1(24)	0.402-2.432	1.220 ± 0.419 (34)	21	0.236-1.192	0.703 ± 0.30 (43)	13	-	-	0
8C1(12)	0.925-2.602	1.514 ± 0.679 (45)	10	0.241-1.116	0.573 ± 0.26 (46)	8	1.000-1.359	1.179 ± 0.25 (22)	2
9C1(3)	1.005-1.816	1.291 ± 0.45 (35)	3	0.066-0.565	0.354 ± 0.26 (73)	3	-	-	0
10C1(1)	-	1.168	1	-	0.418	1	-	-	0
	Overall:	0.328-39.342 (~ 120:1)		Overall:	0.066-21.199 (~ 320:1)				

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* From Pellizzari et al. (1982).

[a] RTI data.

[b] Martelli et al., 1981.

[c] N = number of PCB isomers included in measurement.

[d] All values are relative to octachloronaphthalene.

[e] Responses were relative to lowest response for each group.

[f] ( ) = number of theoretical isomers possible.

Flame ionization detection--Flame ionization detection (FID) is the most commonly used GC detector because of its sensitivity and universality. Although some investigators have used FID for PCB determination in samples, it has generally been used only for calibration of response factors or other method development work.

FID has been used for determination of PCBs in environmental samples (Mizutani and Masayoshi, 1972; Modi et al., 1976; Lao et al., 1976; Onsuka and Comba, 1978). Biros (1971) split the GC effluent to FID for quantitation and EIMS for identification. Cook et al. (1978) and Zimmerli (1974) used FID to detect biphenyl following dehydrochlorination of PCBs; a technique termed carbon skeleton chromatography.

Most of the FID applications have been in establishing response factors, characterizing Aroclors, or other method development areas (Webb and McCall, 1972; Ugawa et al., 1973; Dexter and Pavlou, 1976; Boe and Egaas, 1979; Albro and Parker, 1980; Albro et al., 1981; Stalling et al., 1982). An example of the use of FID is presented in Table 3, where the molar responses of FID and ECD were compared (Hutzinger et al., 1974; Safe, 1975).

Thermal conductivity (TCD)--Hirwe et al. (1974) used TCD to characterize Aroclor mixtures. This application is similar to many of the FID applications.

Electrolytic conductivity--The Hall (and its predecessor, the Coulson) electrolytic conductivity detector (HECD) has been used often in PCB analysis. It is much less subject to interference from nonhalogenated compounds than ECD and the response is proportional to the number of chlorines. The high limit of quantitation and difficulty of operation are the disadvantages of this detector. Webb and McCall (1973) and Sawyer (1978) used Hall detection in the characterization of Aroclor standards. Serum et al. (1973) used it, ECD, and electron impact mass spectrometry as PGC detectors in analysis of paper products for PCBs and other compounds. Hofstaedter et al. (1974) determined that sulfur compounds in certain petroleum oils gave positive interferences in PGC/ECD determinations of PCBs. Flame photometric, microcoulometric, and Hall detectors were used to characterize the PCBs and interferences. Chesler et al. (1981) characterized oil products in the preparations of National Bureau of Standards standard reference materials for PCBs in oil. They used both ECD and HECD as CGC detectors. The ECD was found to be more sensitive than the HECD by two orders of magnitude and easier to maintain in a noncontaminated state. However, ECD response factors varied for different PCB isomers, whereas the molar response to chlorine which is obtained from the HECD appeared to be constant. The HECD exhibited a wider linearity range and is more selective as it responded only to halogenated compounds.

An interesting, though tangential, use of HECD was presented by Dolan et al. (1972), Dolan and Hall (1973), and Su and Price (1973). By adjusting the HECD operating parameters they selectively detected organochlorine pesticides in the presence of PCB interferences.

Electron impact mass spectrometry--Electron impact mass spectrometry (EIMS) ranks second only to ECD in popularity as a GC detector for PCBs.

Electron impact has been and continues to be the most widely used MS ionization technique. While the chemical ionization (CI) and negative chemical ionization (NCI) techniques are often more sensitive, their operation is more complicated and variation in the spectra and response are higher.

EIMS has been applied to PCB determination using both direct probe and gas chromatography for sample introduction. Early work generally employed the then-exotic technique as a confirmation technique. In recent years, as GC/ EIMS has become more routine, more and more analysts have chosen GC/EIMS as the primary technique.

Review articles--The application of EIMS to analysis for PCBs has been reviewed by Fishbein (1972), Oswald et al. (1974), Hutzinger et al. (1974), and Safe (1975).

Standard methods--As listed in Table 1, several of the standard methods use GC/EIMS, either as the primary analytical technique or as the confirmatory technique.

Primary literature--In 69 articles abstracted, EIMS was used. The applications ranged from confirmation to routine use, from direct probe to CGC, and from Aroclor characterization to analysis of dirty samples.

Among the pioneers, Biros et al. (1970) used CGC/EIMS to determine PCBs in human adipose tissue; Sissons and Welti (1971) used CGC/EIMS in the characterization of Aroclor 1254; and Bonelli (1972) presented PGC/EIMS data for an Aroclor 1254/chlorinated pesticide mixture.

In addition to Sissons and Welti (1971), Webb and McCall (1972, 1973), Ugawa et al. (1973), and Oswald (1974) employed GC/EIMS in characterization of commercial PCB products. Using both electron impact and chemical ionization mass spectrometry, Oswald et al. (1974) were able to differentiate some isomers in complex mixtures from their spectra.

While full spectra provide the most qualitative information, the use of selected ion monitoring enhances the instrument sensitivity and selectivity and simplifies data interpretation. Examples of this technique have been presented by Beggs and Banks (1976), Eichelberger et al. (1974), Martelli et al. (1981), Collard and Irwin (1982), Erickson and Pellizzari (1977, 1979) and Tressl and Wessely (1976). Especially with the more highly chlorinated homologs, several m/z values are available for monitoring. Eichelberger et al. (1974) addressed the criteria for selection--intensity and probability of interference from higher homologs or other compounds.

A compromise between full scan and SIM techniques is mass chromatography. Full spectra are collected and then ion intensity versus file position plots are extracted from the data by the computer. Thus, mass chromatography has the ease of interpretation of SIM but higher LOQs since full spectra are collected. These full spectra are available for qualitative use if needed. Canada and Regnier (1976) presented a technique which used mass chromatography to monitor the ion ratios in the PCB isotopic clusters.

Another compromise technique, limited mass scanning (LMS), involves (as the name implies) scanning the spectrometer only over the mass range of interest (e.g., molecular ion cluster). This permits the spectrometer to spend more time on the ions of interest and thus achieve better sensitivity than the full scan mode. Tindall and Wininger (1980) utilized LMS in their PGC/CIMS analysis of commercial products for incidental PCBs.

Albro and Parker (1980) utilized PGC/EIMS as part of a general analytical scheme for chlorinated aromatic pollutants.

Positive chemical ionization mass spectrometry--Positive chemical ionization (CI) mass spectromery (CIMS) is one of the "soft" ionization techniques which tend to produce fewer fragments. Thus, the spectra are simple and the molecular ion is generally one of the most intense peaks. However, with PCBs, the electron impact spectra generally exhibit good molecular ions, reducing the advantages of CI. Another problem with CI is that the ionization process depends on a reagent gas introduced with the sample into the source. Slight changes in gas pressure, source temperature, and electronic conditions can affect the reaction conditions and thus the spectrum (both fragmentation patterns and overall intensity). Thus, CI is not as reproducible as electron impact, either qualitatively or quantitatively.

Several researchers have utilized GC/CIMS for determination of PCBs. Oswald et al. (1974a), Sawyer (1978), and Cairns and Siegmund (1981) characterized standard samples. Oswald et al. (1974b), Iida and Kashiwagi (1975), Stalling (1976), and Cairns and Jacobsen (1977) applied GC/CIMS to PCB metabolites, environmental samples, and food samples.

Dougherty et al. (1973) reported the use of direct probe positive and negative CIMS for the analysis of human adipose tissues for PCBs. Stalling et al. (1980) reported an HPLC/MS technique for PCBs which is presumed to use the CI mode. This preliminary report speculated that HPLC/MS could be useful as a screening technique for environmental samples.

A related but often defined as separate technique, atmospheric pressure chemical ionization has been reported for PCB determination. Dzidic et al. (1975) reported subpicogram detection of 2,3,4,5,6-pentachlorobiphenyl, and Thomson and Roberts (1980, 1982) used the technique for *in situ* detection of PCBs in clay and soil.

Negative chemical ionization mass spectrometry--Negative chemical ionization (NCI) mass spectrometry (NCIMS) is similar to both CIMS and ECD. The basic difference between negative and positive CI is the polarity of the various voltage potentials in the spectrometer and the detector. Many of the chemical reactions in the NCI source and the ECD are the same. NCI and ECD exhibit similar detection limits and selectivities toward chlorinated compounds, thus the interest in NCI. The reproducibility problems of CI are also present in NCI. The range of response factors found with ECD are also found with NCI. NCIMS, a relatively recent technique, is still considered to be a research technique.

The group led by Dougherty has published extensively on the methods and application of (direct probe) NCIMS (Dougherty et al., 1973; Kuehl et al., 1980; Dougherty et al., 1980; and Dougherty, 1981a, 1981b). The technique is described as rapid and highly selective toward halogenated compounds. The latter advantage reduces the need for cleanup and, according to Dougherty (1981a), permits the analysis without the customary GC separation.

Kuehl et al. (1980) used both CGC/EIMS and CGC/NCIMS to analyze fish samples for a variety of chloroorganics, including PCBs. The electron impact spectra were used for primary identification, although the NCI spectra were also of great value. Figure 9 presents the NCI and electron impact TICs for comparison. The NCI is much more selective toward the halogenated compounds, eliminating the broad hump which is presumably a complex mixture of lipids and oils from the fish matrix.

Pellizzari et al. (1981) have used CGC/NCIMS for analysis of PCBs and have characterized the instrument operation parameters. The choice of reagent gas and its pressure markedly affect the relative intensities of the major peaks (m/z 35 and 37, molecular ion, etc.).

The response factors for several PCB congeners are presented in Table 4 (Pellizzari et al., 1982). As with ECD, the range of the response factors is broad. This would probably make quantitation by extrapolation from a single calibration isomer inaccurate.

While not directly used for PCB determination, CGC/atmospheric pressure negative chemical ionization mass spectrometry was shown to be both sensitive and selective for PCDDs in the presence of PCBs (Mitchum et al., 1982). With proper selection of masses and ionization conditions, this technique may be highly selective for PCBs.

High resolution electron impact mass spectrometry--HREIMS is capable of obtaining precise and accurate mass measurements of a peak. This known mass can correlate with only a few possible molecular formulas. As reviewed by Safe (1975), HREIMS is particularly useful for chlorinated compounds because the chlorine mass defect clearly distinguishes a halocarbon from a molecule containing only carbon, hydrogen, nitrogen, and oxygen. Safe (1976) and Safe et al. (1975) have reported the application of HREIMS to the analysis of crude goat urine extracts and other biological samples for PCB and PCT metabolites. The reported 10-ppb detection limit and the rapid analysis time (no GC separation is used) would appear to make this technique a suitable technique for rapid screening of samples for the presence of PCBs. The lack of work in this area, however, suggests that other considerations must reduce the applicability of HREIMS.

Hass and Friesen (1979) illustrated the need for HREIMS to separate interferences (if not chromatographically separated). The spectrum in Figure 10 shows that DDE, TCDD, and PCB would have given one peak under low resolution conditions.

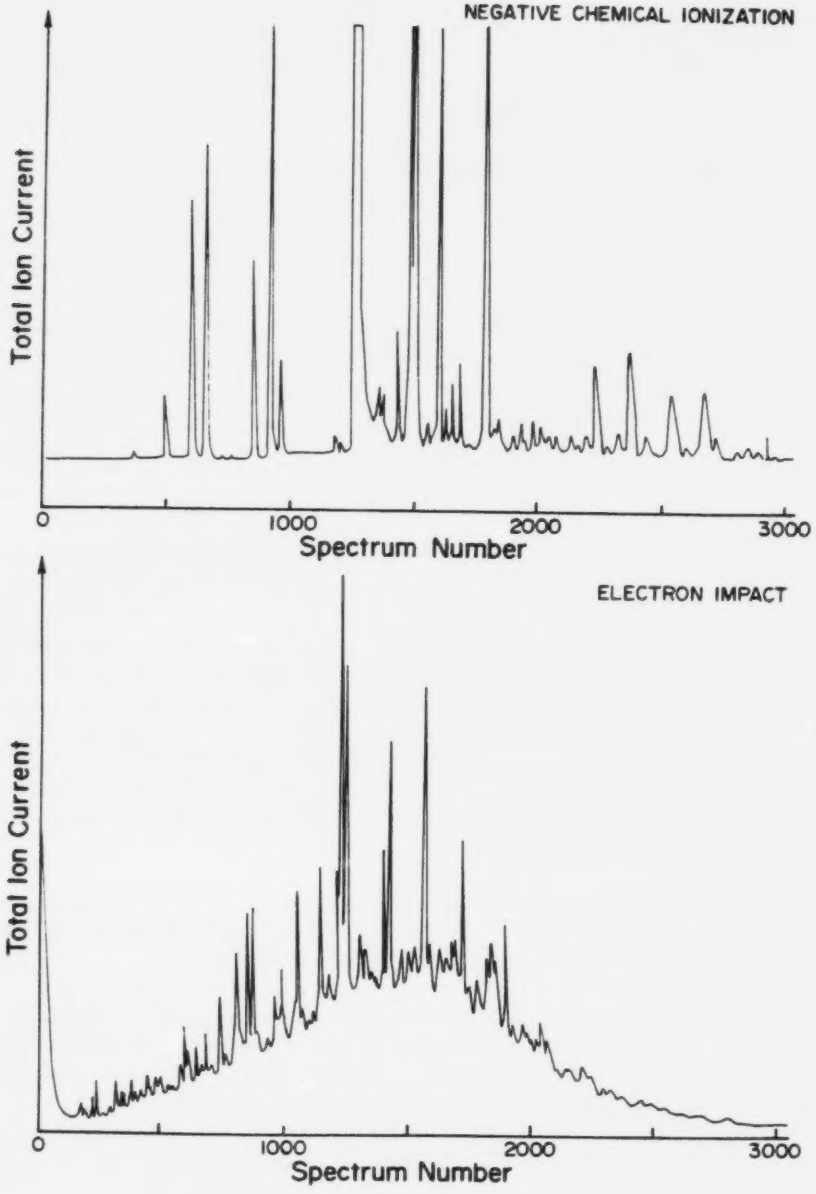

Figure 9. Total ion current profiles for negative chemical ionization data (upper) and electron impact data (lower) obtained on a Finnigan 4000 glass capillary GC/MS system for Ashtabula River fish sample (Kuehl et al., 1980).

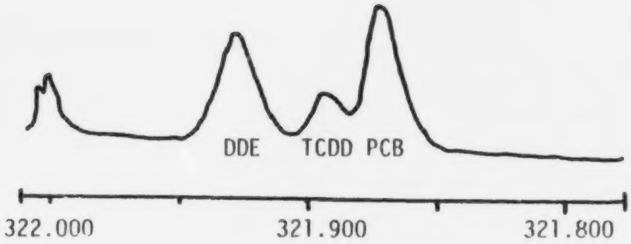

Figure 10. Partial high resolution mass spectrum obtained from 2.5×10^{-10} g TCDD plus matrix from 10 g human milk, illustrating potential interferences in low resolution mass spectrometry (Hass and Friesen, 1979).

Nonchromatographic Methods--

This section presents a variety of miscellaneous methods reported for the determination of PCBs.

Nuclear magnetic resonance (NMR) spectrometry--Wilson and Anderson (1973) used both ^{13}C and ^{1}H nuclear magentic resonance (NMR) to characterize the chemistry of selected PCBs. No attempt at analysis of real samples was made. Levy and Hewitt (1977) reported the analysis of PCB mixtures by ^{13}C NMR, but noted that the technique was not as useful for higher homologs. Hutzinger et al. (1974) included a discussion of the NMR characteristics of PCBs in their review book. Synthetic congeners have been characterized by proton NMR (Mullin et al., 1981).

Infrared (IR) spectrometry--Hutzinger et al. (1974) discussed the infrared (IR) spectral properties of PCBs. Webb and McCall (1972) used IR and other techniques to identify 24 PCB congeners in Aroclor 1221.

Radioimmunoassay--Albro and coworkers have reported preliminary results in the development of a radioimmunoassay (RIA) method for PCBs (Albro et al., 1979; Kohli et al., 1979; Luster et al., 1979, 1981). Suggestive evidence is presented indicating the feasibility of employing radioimmunoassays for determining the Aroclor product number and concentration in environmental samples (Luster et al., 1979). The assay requires an antiserum for each isomer but is termed fairly specific.

Other techniques--Interrupted-sweep voltametry has been applied to the identification of PCBs, yielding positive identifications (Farwell et al., 1975). Plasma chromatography has been reported to give characteristic qualitative data for PCBs (Karasek, 1971). One report utilized neutron activation analysis for the determination of PCBs in dosed rats (Mamri et al., 1971).

identification and quantitation of PCBs (EPA, 1972; Brownrigg et al., 1974; Brownrigg and Hornig, 1974). The limit of detection was reported to be as low as 0.01 ppm.

DATA REDUCTION

Depending on the detection and output system, data may be presented to the analyst as strip chart recorder chromatograms, digitized chromatograms, numerical peak integrations, mass spectra, MS selected ion monitoring plots, MS total ion current plots, etc. Computers can easily reduce the analyst's work in data reduction and should be used for MS data acquisition and reduction. However, excessive reliance on data system output without interaction by a qualified analyst can yield spurious results.

The first task in data reduction is to qualitatively identify the analyte. Quantitation can be attempted only after a positive qualitative identification.

Qualitative

The qualitative aspects of the analysis are all too often overlooked. Especially with PCBs, differences in the qualitative assessment of a sample can dramatically affect the quantitative results. In standard methods or other work where two or more analysts are expected to produce comparable results, the qualitative assessment of the data must be carefully specified.

As an example of how qualitative interpretation of results can affect quantitation, a round robin study was recently conducted to assess the interlaboratory variability of PCB analysis in commercial products (Pittaway and Horner, 1982). Eleven data sets, generated by PGC/ECD, PGC/ EIMS, PGC/EIMS SIM, CGC/EIMS, and PGC/FID, were acquired (see Tables 5 and 6). While most of the techniques were sufficiently specific to differentiate PCBs from interferences, the PGC/FID was not. Since no attempt was made by the analyst to differentiate PCBs from interferences in this case, the PGC/FID quantitation was 28 times higher than the mean of the other analyses.

Qualitative assessment of results depends to a large extent on sample type and its pretreatment. In samples where the presence of PCBs has been well-established (e.g., adipose tissue) the qualitative burden is not nearly so great as for samples in which PCBs are not expected. In many PCB procedures, the cleanup involves a rather specific liquid chromatographic separation which separates PCBs from most organochlorine pesticides. In addition, the use of specific detectors (ECD, HECD) reduces the probability of interferences and increases the confidence in identification. Better still, MS provides spectra of the eluent which may be compared with those of authentic compounds to give high confidence identifications. Finally, the retention time of the eluent should match that of a standard. CGC, and better yet high precision CGC, gives much more precise retention times than PGC and increases confidence.

In the case of Aroclor (or similar mixtures) derived PCBs, a pattern of isomers usually resembles the pattern of a standard. This has been a common qualitative technique in residue analyses, especially when PGC/ECD is the analytical procedure.

TABLE 5. SUMMARY OF LABORATORY TECHNIQUES USED FOR THE CMA ROUND-ROBIN STUDY (Erickson, 1982)

Lab	Work-up technique	Analysis technique	MS calibration method	GC calibration method	Integration technique	Calculation equations	LOD presented
A	DI[a]	PGC/EC[b] PGC/EIMS[d]	Confirmation only	?	PH[c]	No	Yes
B & J	Dil/Inj[e]	PGC/EIMS SIM[f]	Autotune	EG[g] (3 pts)	Areas[h]	Yes	Yes[i]
C	Sonication/Inj (some diluted)	PGC/MS[j]	PFTBA[j]	ES	Ion Intensities	No	Yes
D	Sonication/Inj (some diluted)	PGC/FID	-	ES	?	No	Yes
E	DI and Dil/Inj	PGC/MS[j] SIM	PFTBA	ES (3 pts)	Areas	No	Yes
F	Heat/Inj; Dil/Inj; DI	PGC/EIMS SIM	?	ES, RF[k]	Area	No	Yes
G	DI	PGC/EIMS SIM	?	ES (1 pt)	Area	Yes	Yes
H	Dil/Inj	PGC/EIMS SIM	?	RF	Area	Yes	Yes
I	Dil/Inj	CGC[n]/EIMS SIM	?	RF	Area	Yes	Yes
K	Acid Digest/ Extract/Inj; Some heated	CGC/MS[j]	DFTPP	IS, RF[o]	Summed Area[p]	No	No

See footnotes for Table 6.

TABLE 6. SUMMARY OF LABORATORY TECHNIQUES USED FOR THE CMA ROUND-ROBIN STUDY (Erickson, 1982)

Lab	No. ions/homolog	Isotope ratio mentioned	Reporting units	QA discussed?	No. standard isomers	Comments
A	?	?	ppm	No	18	Too many significant figures. Very little discussion.
B & J	1	No	mg/kg	Yes	24	Some full scan confirmation; good discussion, good work overall.
C	1	No	mg/ℓ; ppm	No	10	Sample preparation is good.
D	-	-	mg/ℓ; ppm	No	5	Major interferences suspected--no caveats or discussion of divergent data with "Lab C."
E	3	Yes	µg/g (?)	Yes	25	No individual isomers reported.
F	2[l]	No	µg/g	Yes	10[m]	Standard addition attempted but failed; use of Aroclor mixtures as standards is of dubious value.
G	4-5	Yes	ppm	Yes	20	Good ion/retention time table; % recovery calculated from standard addition (were results corrected?)
H	1	No	ppm	No	10	H and I are same organzation; no discussion of differences observed in two methods.
I	1	No	ppm	No	10	
K	> 3[q]	No	ppm	Yes	12	Limited recovery study (∼ 100% recovery); injection precision measured for one sample.

FOOTNOTES FOR TABLES 5 AND 6

a Direct injection.

b Packed column GC/electron capture detector.

c Peak height.

d Packed column GC/electron impact mass spectrometry (full scan).

e Dilute and inject.

f Selected ion monitoring.

g External standard.

h Details presented--two integration methods used, one designated "B"; one designted "J."

i Estimated, no details.

j Unspecified operating mode.

k Response factor.

l One ion from parent cluster and one ion from fragment cluster.

m Aroclor mixtures.

n Capillary column GC.

o Internal standard (details unclear).

p Areas of three (two for $C_{10}H_9Cl$) most intense ions in parent cluster summed.

q Limited scan technique used; all ions in parent cluster were observed.

Review Articles--

Only five reviews mentioned the qualitative aspects of PCB analysis (Reynolds, 1971; Sherma, 1975; Safe, 1976; Fuller et al., 1976; and Margeson, 1977). Generally, the qualitative discussion was cursory. Reynolds (1971) advised use of pattern recognition (against the Aroclor standards). Sherma (1975) recommended a slightly more formal approach--comparison of retention times in samples and standards.

Standard Methods--

As noted in Table 1, less than half of the standard methods discuss qualitative analysis. In the PGC/ECD methods pattern recognition is the qualitative procedure. Often chromatography on two GC colums of different polarity is used to enhance the confidence of the verification. An example of good qualitative guidance for the analyst is found in the EPA protocol for analysis of PCBs in transformer fluids and waste oils (EPA, 1981).

> Locate each PCB in the sample chromatogram by comparing the retention time of the suspect peak to the retention data gathered from analyzing standards and interference free Quality Control Samples. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for each PCB can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

In methods where GC/EIMS is specified, both mass and retention time may be used for identification. None of the standard methods adequately address the selection of ions and the permissible abundance ratios.

Primary Literature--

Less than half of the 38 articles abstracted contained mention of the qualitative criteria used in identification of PCBs. A representative qualitative criterion was that the chromatogram exhibits a "typical Aroclor pattern" (Gordon et al., 1982; Giam et al., 1972; Ofstad et al., 1978; Kirshen, 1981).

Several publications dating back to the landmark work of Sissons and Welti (1971) concentrated on the identification of PCB isomers in commercial (Aroclor, Chlophen, etc.) mixtures (Tas and deVos, 1971; Tas and Kleipool, 1972; Armour, 1972; Willis and Addison, 1972; Paasivirta and Pitkänen, 1975; Jensen and Sundström, 1974; Stalling et al., 1978; Neu et al., 1978; Zell et al., 1978; Ballschmiter and Zell, 1980; Pellizzari et al., 1981; Tuinstra et al., 1981). The objective of most of these papers was to characterize the commercial mixture as an aid to quantitation in environmental samples or for toxicological information.

Several researchers mentioned the comparison of retention times or relative retention time in the sample and an Aroclor standard for PCB identification (Webb and McCall, 1972; Onsuka and Comba, 1978; Pellizzari, 1982;

Tuinstra et al., 1980). A much more specific identification scheme involves use of one of the retention index (RI) (e.g., Kovats) schemes. Several publications contain tabulations of RIs (Sissons and Welti, 1971; Zell et al., 1978; Neu et al., 1978; Ballschmiter and Zell, 1980; Albro et al., 1981; Albro and Fishbein, 1972a, 1972b). Since all 209 PCB congeners are not available, a scheme of predicting RIs has been developed based on the half-RI values for the various chlorination positons on one of the benzene rings. Sissons and Welti (1971) first proposed this system, which was expanded upon and further validated by Albro and Fishbein (1972) and Albro et al. (1977). The use of half RIs permits the analyst to qualitatively identify all 209 PCBs on the basis of their retention time, although the level of confidence in this identification is low. Using state-of-the-art chromatography, RI measurement precision of ± 0.05% has been reported for PCBs (Neu et al., 1978), and with full optimization, precision of ± 0.01% has been predicted (Neu and Zinburg, 1979).

Recently Dunn et al. (1982) used a computerized pattern recognition technique to evaluate CGC/ECD data on PCBs in sediments, water, benthos, and fish. The computer program can detect incorrect assignments (i.e., Aroclor 1242 instead of 1260) and abnormal samples. This appears to be a most promising technique for interpretation of large numbers of PCB determinations.

When a mass spectrometer is used as the GC detector, an additional qualitative dimension is available. The mass spectra of a PCB are distinctive due to the cluster of masses generated by the presence of two chlorine isotopes in nature. If sufficient material is present to obtain full mass spectra, the unknown can be reliably identified by comparison with spectra of standards or spectral compilations (Stenhagen et al., 1974; Mass Spectrometry Data Centre, 1970; Heller and Milne, 1978). The quality of the spectrum required for identification needs to be defined (Christman, 1982).

As mentioned above, the natural isotopic abundance ratios yield a characteristic pattern. The use of these ratios in selected ion monitoring can provide qualitative information when full mass spectra are not obtained. The actual ratios have been tabulated for PCBs (Rote and Morris, 1973) or may be readily calculated. This approach has been utilized (Canada and Regnier, 1976) with complex samples (Erickson and Pellizzari, 1977, 1979). Even though the natural isotopic abundance ratios are constant, instrumental variances and interferences can affect the observed ratio. Thus, tolerance criteria need to be utilized by the analyst.

Tindall and Wininger (1980), in a method designed to determine PCBs even if they are not "Aroclor-derived," established qualitative criteria:

> Each peak in the chromatogram is evaluated to determine if it is a PCB peak. Peaks must meet these criteria to be labeled PCB peaks for quantitation: (1) the peaks of the characteristic ions must maximize at the same retention time; (2) the peak must be in the proper retention time window; and (3) the relative peak intensities of the molecular ions must be within ± 15% of the theoretical ratio. This tolerance is arbitrary and can be made larger for very low concentrations of PCBs where statistical variations in peak intensity become large.

Work by Collard and Irwin (1982) and Dow (1981) established similar qualitative criteria:

> Identify the chlorinated biphenyl homologs by their mass ion response, relative retention time, and ion intensity ratio (± 20% relative). Secondary confirmation of trichloro-through decachlorobiphenyl may rely upon the M-70+ ion response.

These two works suggest a new awareness that qualitative criteria must be stipulated in any method if the results are to have any significance.

In addition to the various gas chromatographic identification methods, thin-layer chromatography and high performance liquid chromatography yield qualitative information, as discussed above. More exotic techniques such as other mass spectrometric techniques, Fourier transform infrared spectrometry, and nuclear magnetic resonance spectroscopy are not used routinely in most laboratories, so have been included as confirmatory techniques which will be discussed below.

Quantitative

With most organic compounds, the quantitation is relatively straightforward. The instrumental response is calibrated using standards. The amount of unknown is measured by comparison of the signal it generates with the calibration factor or curve. Quantitation of PCBs is not nearly so simple because the analyte is not a single compound but rather a complex mixture of 209 possible congeners and standards of all 209 congeners are not available for calibration. Given these problems, analysts have devised alternate quantitation methods generally based on the similarity of the sample PCB mixture to a commercial product (e.g., Aroclor).

Review Articles--

Most review articles mention quantitation of PCBs briefly. Safe (1976) discussed the problems of ECD response variability discussed in detail above and suggested that perchlorination would be more consistently accurate. Hutzinger et al. (1974) reviewed the quantitation methods to that date, most of which involved relating the unknown to Aroclor standards. Sherma (1975) provided a similar, but more detailed, review which included a positive assessment of the Webb and McCall (1973) procedure. The other reviews (Riseborough, 1971; Fuller et al., 1976; Reynolds, 1971; Margeson, 1977) discussed quantitation in similar but less detailed fashion.

Standard Methods--

As shown in Table 1, all standard methods give at least cursory instructions on quantitation. At one extreme, the general purpose protocols (EPA, 1979a, 1979b; Ballinger, 1978; EPA, 1978) contain vague direction to "integrate the area under the peak." Much more complete quantitation guidelines are given in EPA's (Bellar and Lichtenberg, 1981; EPA, 1981) protocol for analysis of PCBs in transformer fluids and waste oils.

Primary Literature--

It is obvious from the data presented that PCBs were quantitated in most of the references abstracted. However, many articles neglect to mention how the PGC/ECD signal was converted into a concentration value. Some 80 articles abstracted mentioned the quantitation technique, although many only made a brief mention of "integration" or "comparison with Aroclor 1260 standard."

Packed column gas liquid chromatography/electron capture detector--As noted in Table 3, the response factors for the individual PCB congeners vary widely, even within a homolog. This fact has typically been overlooked in quantitation procedures based on the use of Aroclor (or other commercial mixtures) standards.

The most prominent GC/ECD quantitation method was originated by Webb and McCall (1973). The weight percent and homolog identification (relative proportions where more than one homolog was present) were determined for several Aroclors, and retention times relative to p,p'-DDE were specified. The general procedure is as follows:

> Chromatograph known amounts of the standards and measure the area for each peak. Using the tables of data determine the response factor (ng PCB/cm^2) for each peak. Chromatograph the sample and measure the area of each peak. Multiply the area of each peak by the response factor for that peak. Add the nanograms of PCB found in each peak to obtain the total nanograms of PCB present. Samples containing one Aroclor or more than one Aroclor can be quantitated by comparison with appropriate standards.

Following an interlaboratory survey, Chau and Sampson (1975) recommended that the Webb and McCall method be adopted as the uniform quantitation method. They cited the general applicability, elimination of mixed standards, the more realistic results, and simplicity of the method as reasons for their recommendations.

Exact replication of the method requires reproducing the chromatography and using the same lot of Aroclor standards as Webb and McCall used. These stringent requirements have led most researchers to characterize their quantitation practice as a modified Webb and McCall (Erickson et al., 1981; Kreiss et al., 1981; Harris and Mitchell, 1981; Steichen et al., 1980; Sawyer, 1978a). The calculations required can be easily automated using common GC integrators or data systems (Erickson et al., 1981; Kirshen, 1981).

Ugawa et al. (1973) devised a quantitation method similar to a Webb-McCall except it was based on the Japanese commercial PCB, Kanechlor.

Unfortunately, most samples are exposed to weathering, metabolism, differential adsorption, etc., and the PCB pattern, though originally one or more Aroclors, does not closely resemble that of the standard. This has been noted repeatedly and certain correction procedures have been proposed (Beizhold and Strout, 1973; Webb-McCall, 1973).

Several researchers (Collins et al., 1972; Rote and Murphy, 1971; Bellar and Lichtenberg, 1975) and standard methods (AOAC, 1980; ASTM, 1980a, 1980b) advocate comparison of the total areas under the "Aroclor region" in the sample and standard chromatograms. This is a simple approach and has been recommended by Sawyer (1973) as the most reliable method for obtaining interlaboratory precision. In a later collaborative study (Sawyer, 1978b), the individual peak height (Webb and McCall, 1973; Sawyer, 1978a), total peak height and total peak area methods were all compared and gave similar results, although the individual peak method was judged slightly better. On this basis, AOAC (1980) permits either individual peak (Webb-McCall) or total area quantitation of PCBs. Bellar and Lichtenberg (1975) used either the total peak height for samples closely resembling Aroclors or Webb-McCall for patterns "not representing a single Aroclor."

Wolff et al. (1982) used 2,4,4'-trichlorobiphenyl, 2,4,5,2',5'-pentachlorobiphenyl; and 2,4,5,2',4',5'-hexachlorobiphenyl as standards for CGC/ECD quantitation of PCBs in plasma and adipose samples of occupationally exposed people. Quantitation by this sum of individual peaks method gave comparable results to the Webb-McCall method using PGC/ECD. Both methods gave lower values than the sum of peak areas method using PGC/ECD data.

Zobel (1974) devised a computer fit routine which matched the sample chromatogram with various "co-added" Aroclor chromatograms to obtain a best fit. "Spuriously large or small peak heights, caused by interfering compounds or metabolism, are automatically sorted and rejected." The method reports results in terms of the different Aroclors and can be modified to generate an estimate of "premetabolism" PCB content.

While providing no details on how the PCBs were quantitated, Giam et al. (1973) required at least 50% of the peaks in the sample chromatogram to match those in an Aroclor standard when analyzing marine biota for PCBs.

Capillary column gas liquid chromatography/electron capture detection--The application of CGC to PCB determination complicates the already difficult quantitation problems: more peaks are present. Since the peaks are ostensibly single congeners instead of the mixture obtained by PGC, much emphasis has been placed on quantitation of single congeners. Boe and Egaas (1979) devised a calibration factor system that permits the analyst to calculate the ECD response factor for a given congener, once its structure is known. More recently, the response factors for 159 congeners were measured (Table 4). As discussed above, the ranges over homologs and within a homolog indicate that calibration with each congener would be necessary for accurate results.

Despite the higher resolution with CGC and therefore more available information, simplistic quantitation routines are still used. Gordon et al. (1982) used three peaks from each Aroclor standard as their method for quantitating PCBs in transformer oil by CGC/ECD. While PCBs do not weather extensively in transformer oil and are thus more likely to resemble the parent Aroclor, this method utilizes only a small portion of the available information. Schulte et al. (1976) recommend quantitation of CGC/ECD chromatograms based on two selected charactistic peaks in food extracts.

Albro et al. (1981) determined the relative molar percentages of the individual components of about 100 different PCB congeners in Aroclors 1248, 1254, and 1260. They recommend using the Aroclor mixtures as secondary standards to calibrate CGC/ECD responses.

Gas liquid chromatography/electron impact ionization mass spectrometry--The ability of EIMS to easily sort PCBs by homolog has led to a tendency among GC/EIMS users to quantitate by homolog (e.g., summing all homolog peaks). Another major difference from analog (ECD) detector quantitation is the ability to quantitate using either a single PCB-specific m/z peak or the total ion current which corresponds to the analog detector output.

The first reported GC/EIMS quantitation was a simple translation of classical PCB GC/ECD quantitation: comparison of "the area under one or more of the eight peaks to the area of a known amount of a standard" (Bonelli, 1972a,b).

Eichelberger et al. (1974) chose what they termed the conventional approach and assumed that the PCB mixture was identified as one of the commercial mixtures. The total peak area for each SIM mass in the sample and standard were compared using an internal standard to normalize the peak areas.

Erickson and Pellizzari (1977, 1979) quantitated PCBs in sludge based on a relative molar response (RMR) of each homolog. Using SIM techniques, the RMR for one isomer of each homolog was determined. Standards of hepta- through monochlorobiphenyl were too impure to use and RMRs for these homologs were interpolated. The RMR decreased dramatically (logarithmically) with increasing degree of chlorination, presumably due to the decreasing ionization cross-section.

Williams and Benoit (1979) compared the summed total integrated area for six to eight selected peaks in samples and standard for quantitation of PCBs in several household products.

Tindall and Wininger (1980), in one of the few papers addressing analysis of non-Aroclor PCBs, established homolog response ratios using an unspecified number of isomers per homolog. The highest and lowest response factors for a homolog were averaged to give the average response factor used in the calculation of PCB concentration in the unknown. An internal standard (tribromobiphenyl) was used to get relative responses.

Martelli et al (1981) reported the EIMS relative response factors for 45 PCB congeners (Table 4). The relative standard deviation per homolog ranged from 0.7% (3 of 46 isomers) to 21% (11 of 42 isomers). They propose using these average response factors on GC/EIMS quantitation of PCBs by homolog.

Collard and Irwin (1982) used an unspecified number of isomers per homolog to establish response factors for each homolog. A daily calibration plot at three concentrations was used for comparison of the summed peak heights for one homolog.

Dow (1981), in a related protocol, specified 22 congeners to be used in a similar calculation. For homologs with more than one isomer in the standard a summed intensity was used.

Miscellaneous--Cairns and Jacobsen (1977) advocated the quantitation of PGC/EIMS because of the reduction in interferences by other halogenated compounds such as DDE. Eichelberger et al. (1974) also mentioned PGC/EIMS as an alternate technique for dirty samples but did not discuss quantitation.

As discussed in a separate section, perchlorination and dehydrochlorination, followed by PGC/ECD and PGC/FID determinations, respectively, have been proposed as PCB quantitation methods which eliminate the congener variability problems.

TLC and HPLC have also been employed as quantitative techniques and are discussed in separate sections above.

CONFIRMATION

Confirmatory techniques have been frequently used in PCB analysis. The term confirmation may be loosely defined as any operation performed to increase the confidence of the results beyond the primary analysis. Qualitative confirmation is much more often reported than quantitative confirmation. Confirmatory techniques involve variation of the same technique (PGC/ECD on two dissimilar columns), confirmation by a lesser technique (PGC/ECD with TLC confirmation), or confirmation by a more advanced technique (PGC/ECD with PCG/EIMS confirmation).

Review Articles

Hutzinger et al. (1974) devoted about two pages to the subject of confirmation. While mass spectrometry was briefly mentioned, most of the discussion centered on perchlorination.

Standard Methods

Table 1 listed all of the standard methods and notes the type of confirmation suggested. All of these confirmations are optional and qualitative.

Primary Literature

As early as 1969, the need for confirmation of findings was discussed (Reynolds, 1969). An exchange of comments following a presentation by Riseborough (1971) led to a proposal for confirmation by P. L. Diosady, covering, mass spectrometry, dechlorination, and perchlorination. Price and Welch (1972) are typical of many early investigators who backed up their PGC/ECD analysis with a TLC confirmation (see also the standard methods: AOAC, 1980; FDA, 1977). Hannan et al. (1973) utilized a cumbersome ultraviolet irradiation method to confirm PGC/ECD results.

Mes and coworkers have utilized a variety of confirmatory techniques, generally in concentration, in the analysis of adipose and milk samples (Mes et al., 1977; Mes and Davies, 1979; Mes et al., 1980). The methods include two dissimilar GC columns, perchlorination, and GC/EIMS.

GC/EIMS was used by Biros et al. (1972) to confirm TLC results. GC/EIMS confirmation has also been reported (Musial et al., 1979; Teichman et al., 1978; Lucas et al., 1979; Rodriguez et al., 1980; Haile and Baladi, 1977; Erickson et al., 1981). HREIMS has been reported as a confirmatory technique (Safe et al., 1975; Safe, 1976; Musial et al., 1974). Kuehl et al. (1980) used CGC/NCIMS to qualitatively confirm their CGC/EIMS PCB identifications in fish. Hass and Friesen (1979), placing particular emphasis on polychlorinated dibenzodioxins, reviewed the advanced mass spectrometric techniques for both high sensitivity and high reliability analysis: HREIMS and NCIMS.

SCREENING TECHNIQUES

Screening techniques in this text are defined as methods used to identify the presence of PCBs qualitatively, semiquantitatively, or quantitatively without specification of the homologs in a sample extract. Screening techniques under this definition could include thin-layer chromatography, high performance liquid chromatography, and gas-liquid chromatography. These methods have been discussed in detail earlier in this review. Perchlorination and carbon-skeleton chromatography, however, are screening methods that have not been mentioned, although Table 1 indicates that perchlorination has been used as a quantitative method or PCB confirmation technique in several of the standard procedures.

Perchlorination

Perchlorination methods are based on the exhaustive chlorination of the biphenyl ring of the PCB congeners. The major disadvantage of the perchlorination reactions is that biphenyl can also be perchlorinated. Thus, the presence of biphenyl can lead to erroneously high levels of quantitation. Quantitative analysis is typically accomplished by GC/ECD systems although GC/MS identification has been used in some instances. Perchlorination reactions are reportedly troublesome because of contamination of reagents with decachlorobiphenyl or brominated compounds (Trotter and Young, 1975).

Perchlorination reaction methods were first studied using antimony pentachloride (Berg et al., 1972; Matsumoto, 1972; Armour, 1973) and thionyl chloride in the presence of aluminum chloride (Nose, 1972). Armour (1973) reported greater than 90% recovery of PCBs by perchlorination and found the technique comparable to PGC/ECD comparison with Aroclor standards. Nose (1972) reported approximately 100% conversion of tri-, tetra-, and hexachlorobiphenyls to decachlorobiphenyl with the thionyl chloride system. Antimony perchloride is apparently the most frequently used reagent as indicated by a review of the literature. Hutzinger et al. (1973) studied trichlorosulfur-tetrachloroaluminate to quantitatively convert Aroclor 1254 to decachlorobiphenyl. One of the major disadvantages of perchlorination arises from blank problems (Trotter and Young, 1975). This has resulted in the need to carefully characterize perchlorination reagents prior to reaction (Huckins et al., 1974). The other major disadvantage of perchlorination is the conversion of biphenyl to decachlorobiphenyl. Chlorine-37 labeled perchlorination reagents have been studied as a means to clarify this problem and at the same time distinguish the contribution of various PCB homologs to the final decachlorobiphenyl by computer assisted isotope dilution interpretation (Burkhard and Armstrong, 1982). This technique, although unique in approach, requires optimum reaction and MS conditions for successful analysis. Perchlorination has been used successfully for numerous studies in recent years (Kohli et al., 1979; Sherma, 1981; Stratton et al., 1978; Fulton et al., 1979; Crist and Moseman, 1977; Robbins and Willhite, 1979; Mes et al., 1977; Mes and Davies, 1979; Haile and Baladi, 1977; Vannuchi et al., 1976; Margeson, 1977; Brinkman et al., 1978; Kohli et al., 1979; Albro et al., 1980; Leoni et al., 1976; Trevisani, 1980).

Carbon Skeleton Chromatography

Carbon skeleton chromatography is based on the dechlorination of PCBs to biphenyl. Catalysts for the dechlorination are typically platinum or palladium. The disadvantage of carbon skeleton chromatography is that background levels of biphenyl in the sample extract will yield erroneously high concentrations of total PCBs as noted for perchlorination. Also, since the product of dechlorination is biphenyl, mass spectrometry must be used to reliably identify the compound, especially in extracts from complex matrices.

Quantitative carbon skeleton chromatography by catalytic decomposition of the PCBs over platinum or palladium to biphenyl has been discussed in three articles (Berg et al., 1972; Zimmerli, 1974; Cooke et al., 1978). Zimmerli (1974) and Cooke et al. (1978) studied conversion of PCBs as well as halogenated terphenyls, napthalenes, dioxins, furans, and DDT. Effective catalysts were found to be effective as 3% palladium at 305°C and 5% platinum at 180°C. Reaction products for the various compounds were identified by GC/MS. On the other hand, false negative results have been observed using this technique for analysis of chlorinated bottoms (personal communication, M. D. Crouch, Toxicon Laboratories, Baton Rouge, Louisiana, 1982).

QUALITY ASSURANCE

A strong quality assurance (QA) program for PCB analysis should include use of pure standards, solvents, and glassware; an evaluation of method blanks for background PCB and interference levels; calibration of instrumental equipment; validation of the individual method steps as well as the overall method; and an evaluation of the overall performance of a method through replicates, interlaboratory comparisons, and/or standard reference materials. The data that should be provided by a strong QA program should include at a minimum, precision and accuracy measurements for each sample matrix.

These parameters have been previously outlined by MacDougall et al. (1980) in an attempt to clarify needs for general data quality evaluation for comparison of trace organic results among numerous laboratories. The guidelines for data acquisition and data quality evaluation presented by MacDougall et al. (1980) were provided under the direction of the Americal Chemical Society Committee on Environmental Improvement and the Subcommittee on Environmental Analytical Chemistry. The guidelines were based on good analytical practices to assist analysts in obtaining data of requisite quality and to aid in the evaluation of the quality of the reported data. In addition to the QA parameters previously listed, MacDougall et al. (1980) have presented requirements for sampling to adequately characterize a sample and enhance reliability in the final result. These guidelines also discuss the necessity of detailed documentation of sample preparation and actual analysis such that other qualified analysts may duplicate the work. The demonstration of precision and accuracy of measurements through good laboratory practices, proven methodologies, low noise instrumentation, the use of standard reference materials, and participation in collaborative studies were also discussed as essential to strong QA programs. The guidelines also presented definitions of and criteria to establish limits of detection (LOD) and limits of quantitation (LOQ). Method validation, qualitative confirmation of validated measurements, risks in data interpretation from low recovery methods, reporting of interferences, and the appropriate presentation of the analytical results were discussed with respect to evaluation of data quality.

Quality assurance in some form has been practiced in many of the studies abstracted for the PCB analysis literature review. However, few of the studies have implemented enough QA to allow comparison of the data from one matrix to the next.

The EPA has taken steps to implement strong QA programs in various standard methods of analysis and as part of long-term project goals (EPA, 1979a, 1980a, 1980b, 1981; Bellar and Lichtenberg, 1981). Table 1 lists the standard methods that acknowledge the need to follow some type of QA program. Other than the standard methods and EPA guidelines, QA programs have been practiced for collaborative method studies for PCBs in different matrices (DCMA, 1981; Sawyer, 1973, 1978; Delfino and Easty, 1979; Devenish and Harling-Bowen, 1980).

The QA program for the Dry Color Manufacturers Association (DCMA, 1981) round robin study included instrument calibration specifications, performance evaluation of the gas chromatography column with a standard mixture of PCBs, and measurement of sensitivity for PCBs by serial dilution of the standard, methods blanks, specification of quantitation procedures and validation of sample preparation procedure. The validation of sample extraction, cleanup and analysis included workup of blind and known spike samples. The results of the DCMA study indicate that variance in reported PCB levels between laboratories was signficantly reduced when a commercially prepared quantitation standard was used by all participating laboratories. Data from the DCMA report indicated relative standard deviations of 3.1 to 9.1% within a laboratory, 2.4 to 40% between laboratories, and values ranging from 7.3 to 41% representing the total reproducibility for analysis of three different pigments.

The Chemical Manufacturers Association sponsored a round-robin study of PCB concentrations in five different samples that are indicative of matrices that will be regulated by the PCB Remand Rule (Pittaway and Horner, 1982). Eight different laboratories participated in the study. In contrast to the DCMA study, no defined protocol or QA programs were specified for analysis of the matrices. Each laboratory was allowed to choose the method of extraction, cleanup, instrumental determination and quantitation, and QA program if desired. This study indicated that there are many sources of potential error in the quantitative analysis of PCBs. A comparison of the reported levels of PCBs and precision of measurements between laboratories indicated a true need for a strong QA program that might allow some normalization of the data.

The collaborative study reported by Delfino and Easty (1979) focused on the analysis of PCBs in paper mill effluents. The study consisted of two phases. The first phase was used to determine the comparability of PCB methodologies between six different laboratories and the abilities of the participating analysts to perform the basic operations required for PCB analysis. These factors were determined by direct injection and quantitation of a performance standard and the simple extraction and analysis of a spiked aqueous solution. The second phase required an actual validation of a sample method using known and blind samples. A modified EPA wastewater analysis protocol was followed by all participating laboratories. Some flexibility to the method protocol was allowed for column materials and exact quantitation procedures. The results of the first phase extraction from distilled water yielded an average recovery of 95.6% with a relative standard deviation of 14.7%. The relative standard deviation for direct injection of a standard solution was 15.6%, thus indicating that gas chromatographic analysis was the principle source of variance. The results for paper mill effluent yielded similar results with 93.6% average recovery with a 16.0% relative standard deviation, and indicated that the method was satisfactory for paper mill effluents.

Sawyer (1978) conducted a collaborative study of PCB quantitation with ECD as the detector. Ten independent laboratories took part in the study and used existing AOAC methodology to study three ECD quantitation procedures. The average combined recovery in this study was approximatley 85% with a coefficient of variation of 15%. No significant difference was noted for the three different quantitation operations.

A large void in most QA programs has been filled by the provision of standard reference materials of known PCB concentration (Chesler et al., 1982). Although the standard reference material will only be available as an oil, it leads the way in establishing further QA criteria for the analysis of PCBs in other media. The preparation of additional PCB standard reference materials as wet and dry reference materials has been discussed by Chau and Lee (1980), Chau et al. (1979), and Addison and Nearing (1982), although these materials are not currently available.

Other policies that are of considerable concern and reflect the current attitudes toward QA have been presented by Glaser et al. (1981) concerning method detection limits based on confidence levels and the guidelines presented by Environmental Science and Technology (Christman, 1982) outlining information required to label compounds identified by mass spectrometry as "tentative" or "confirmed."

BY-PRODUCT PCB ANALYSES

Historically, analysis of PCBs has been concerned with commercial mixtures, such as Aroclors, and their dispersal in the environment and certain commercial products (packaging materials, paper products, transformer oils, etc.). The analytical approaches to identification and quantitation of these commercial PCB mixtures has already been discussed in this literature review. Health and environmental concerns have resulted in an increasing number of federal regulations (EPA, 1979d) controlling the manufacture, use, and disposal of PCBs. A recent report prepared by the Chemical Manufacturers Association for EPA (Pittaway et al., 1981) documents numerous commercial processes that will be affected by proposed federal regulation of by-product PCBs. These by-product PCBs are produced by diverse processes, few of which resemble the commercial PCB synthesis routes. Thus, the resultant PCB mixtures do not resemble the familiar Aroclors. The analysis of by-product PCBs was reviewed by Hodges et al. (1982).

An extremely limited number of articles are available for review of by-product analysis (Tindall and Wininger, 1980; Collard and Irwin, 1982; Pittaway and Horner, 1982; DCMA, 1981; Dow, 1981). These few references, however, describe some of the problems encountered in by-product analysis of commercial products as discussed below.

Dry Color Manufacturers Association Pigment Analysis

A major study was conducted by the Dry Color Manufacturers Association (1981) for the analysis of by-product PCBs in three different pigments. This study concluded that a universal cleanup procedure was not possible for accurate PCB analysis from all of the pigments. The use of GC/MS was recommended for establishing positive identification of the PCBs. Two of the pigments studied contained only one PCB isomer, while the third pigment was contaminated with several different isomers of the penta- and hexachlorobiphenyl homologs. A thorough quality assurance program was developed for the purpose of reducing interlaboratory variability. The quality assurance program included validation of each step of sample preparation, gas chromatographic performance standards, and mass spectrometer calibration and performance appraisal, as well as requirements for analysis of spiked blanks, replicates, and standard additions.

Round-robin experiments were conducted under this study. The DCMA found that a large portion of the interlaboratory variance was due to the differences in preparation of the standard mixtures of PCB isomers used for establishing response factors. A calibration mixture obtained from a single source was found to greatly reduce interlaboratory variance. In addition, specification of PGC criteria with respect to retention times and resolution of specific isomers was required to promote comparability of results between laboratories.

Chemical Manufacturers Association Round-Robin

The Chemical Manufacturers Association has conducted a round-robin experiment for analysis of by-product PCBs (Pittaway and Horner, 1982) in chlorinated benzene waste streams, mixtures of chlorinated benzenes, blind spikes in the chlorinated benzenes, composite waste streams from a chlorinated aliphatic process, and a benzene column bottom sample. The round-robin studies defined some of the problems of by-product PCB analysis in commercial products and process waste streams.

Many sources of potential error in the quantitative analysis of these samples were identified and include unknown interferences, inappropriate use of reference standards, inappropriate protocols, day-to-day variations in instrumental responses, calibration, and execution of analytical procedures, inappropriate collection of samples, contamination of samples, and limitations in instrumental methods.

The round-robin study measured differences in analytical results between laboratories, differences due to variation in analytical methods, limitations of instrumental methods, and impact of analysis by random laboratories

(Pittaway and Horner, 1982; Hodges et al., 1982). A total of eight laboratories (six industrial and two EPA) participated in the study, using a variety of techniques as shown in Tables 5 and 6. Guidelines were not given for methods of sample preparation, instrumental analysis, quantitation measurements or quality assurance practices. The results from the round-robin study showed a significant variance in data among laboratories, which one might expect from the lack of written protocol and quality assurance. This study demonstrated that there is a need for a common denominator in analytical protocol for analysis of by-product PCBs from a wide variety of simple to complex matrices.

Other Studies

Tindall and Wininger (1980), Collard and Irwin (1982), and Dow (1981) studied PGC/MS methods for analysis of by-product PCBs in commercial and environmental samples. The MS analysis method was based on limited mass scan ranges to qualitatively identify and quantitate any of the possible 209 PCB congeners by homologs. Tindall and Wininger (1980) reported that the criteria for PCB quantitation must include matching of characteristic ions at proper retention time windows. In addition, characteristic ions must maximize at the same retention time and the relative peak intensities must be within ± 15% of the theoretical ratio.

The accuracy limiting step of the PGC/MS (limited mass scan range) methods (Tindall and Wininger, 1980; Dow, 1981; Collard and Irwin, 1982) is the selection of standards. In each case response factors were determined for a limited number of isomers for each PCB homolog with the underlying assumption that all PCBs of the same homolog have nearly the same response factor.

Quantitation procedures varied between the studies. Tindall and Wininger (1980) used an internal standard, tribromobiphenyl, which responded to MS source changes much like a PCB. In addition, its molecular weight was great enough that interferences were rarely encountered. Collard and Irwin (1982) and the Dow method (1981) quantitated versus a calibration curve established at various concentrations using 10 congeners to represent each PCB homolog. No internal standards were used. The accuracy and precision of these PGC/MS methods are dependent on frequency of instrumental calibration and the extent that other compounds in the ion source of the MS affect the sensitivity during the course of an analysis.

SECTION 4

APPLICABLE TECHNIQUES

The objective of this section is to outline the best possible approaches for by-product PCB analysis in commercial products that will be regulated under the PCB Remand Rule. The proposed procedures are a result of the review of the available literature presented in the previous section. The analytical approaches provide versatility in terms of the wide spectrum of matrices represented by the proposed regulated products. The success of the proposed rule will rely heavily on a strong quality assurance (QA) program to monitor sample preparations and instrumental analysis. The proposed QA program will provide sufficient data to determine the quality of the quantitation data for each specific sample matrix encountered. Sample extraction, cleanup, instrumental determination, quantitation and data reduction, confirmation, screening, and the overall quality assurance program are discussed.

EXTRACTION

The literature review of extraction techniques describes several approaches to isolation of PCBs from various matrices. The extraction may be as simple as dilution of an organic liquid, batch extraction of aqueous solutions, or Soxhlet extraction of solids; or as complex as matrix destruction via saponification or with concentrated acid before extraction of the PCBs with an appropriate organic solvent. However, the analyst must keep in mind that totally unexpected reactions produced the trace levels of the by-product PCBs being determined. Hence, the use of vigorous or harsh chemical reactions may generate or destroy PCBs (L. F. Hanneman, Dow Corning Corporation, personal communication, 1982). Suitable organic solvents will include petroleum ether, hexane, and methylene chloride. The exact extraction procedure, however, is dependent on the specific matrix. The alternative to designating a specific extraction procedure for all solid and liquid samples that are of highly dissimilar matrices both chemically and physically is to formulate a rigid QA protocol before the extraction step and to continue it through all aspects of analysis. The QA protocol will require extensive homogenization of samples (solids, suspensions, liquids) by grinding and mixing. An aliquot of each homogenized sample will be spiked with a series of surrogate compounds. Final analysis of the sample extract for the surrogate compound recoveries will provide sufficient quantitative information to evaluate the effectiveness of the extraction procedure and or cleanup technique.

The choice of surrogate compounds is critical for exact performance measures of any method. The surrogate compounds must maintain the exact chemical characteristics of the PCBs for extraction, cleanup, and quantitation purposes. The surrogates may be either a series of PCB congeners representing each of the chlorinated homologs or a selected number of stable mass-labeled (carbon-13 or chlorine-37) PCB isomers. The series of unlabeled PCB congeners surrogates would necessitate independent measures of spike recovery and analyte concentration, whereas the mass-labeled PCB surrogates would allow simultaneous determination and quantitation of the analyte PCBs and the surrogate compounds if EIMS is used as the GC detection. The implementation of the use of the mass-labeled surrogates would provide a strong QA program since recovery could be monitored for each sample analyzed and consistency between analytical laboratories and different sample matrices could be compared more readily by a regulatory agency.

Mass-labeled PCB isomers as surrogates could be provided at a reasonable cost per sample analyzed (W. Duncan, Midwest Research Institute, personal communication, 1982). A series consisting of mono-, tetra-, octa-, and decachlorobiphenyl mass-labeled isomers would provide a sufficient set of surrogates. Carbon-13 labeled isomers of 99% purity for these homologs would provide sufficient differences in mass spectra patterns for differentiation from isomers of natural abundance.

The major problem to consider in adding surrogate compounds is whether the incorporation of these compounds in a matrix will mimic the true analytes. Incorporation cannot always be achieved, especially with matrices that require exhaustive extraction methods. However, the measured recovery of surrogates from an extraction and cleanup procedure will provide information on degradation of PCBs by the analytical procedure.

It may be desirable to design small scale experiments to incorporate the surrogate PCBs during a product process (L. F. Hanneman, Dow Corning, personal communication, 1982). Solid matrices, expecially those that may be intractable, should be of prime interest for this approach. The surrogate compounds could be incorporated before polymerization, vulcanization, curing, precipitation, or other processes. The recoveries of the surrogates could be used to determine if the proposed extraction technique is applicable for routine analysis of particular solid matrices.

Exact extraction protocols could be designated for air and simple aqueous samples as shown in Table 1. Exact extraction protocols for commercial products could also be designated, but optimum performance for all matrices is highly unlikely. A specified extraction protocol would require rigorous methods for all samples and must consider possible adverse reactions of certain products to sulfuric acid digestions and alkaline saponification.

Independent extraction procedures for different matrices combined with the use of surrogate compounds and thus validation of the method would be an effective alternative. Each independent laboratory, however, must certify that an effective extraction procedure is practiced.

The level of recovery considered sufficient and method of addition of internal standards for final quantitation are yet to be determined.

CLEANUP

Many cleanup techniques are applicable to commercial products. The nature of the sample, complexity of the matrix, and the chemical characteristics of other components dictate the requirements for any sample preparation. Cleanup for air and aqueous samples in effluents from commercial production facilities is achievable by applying standard methods (Table 1). However, cleanup of a wide range of product matrices will require application of many different techniques. A generic cleanup procedure may not suffice or be necessary in the majority of analyses because of the different chemical characteristics in the sample matrix. For example, sulfuric acid may provide sufficient cleanup and quantitative recovery of one product that contains only decachlorobiphenyl. However, this procedure will not be sufficient for a matrix that contains mono- through trichlorobiphenyl isomers, which may not be recovered quantitatively. Likewise, designated adsorbent columns may not provide the separation of interferences necessary for good quantitative analysis for a large majority of matrices.

As with the extraction step, one alternative is to allow the individual laboratory to develop the necessary cleanup procedure. Each laboratory, however, must follow the stringent QA program using spiked samples or surrogate compounds to validate the method at a determined level of proficiency. This will meet the special analytical needs of the individual analyst and at the same time provide the data necessary to determine analytical proficiency of the method and consistency between laboratories and matrices.

DETERMINATION

Gas-liquid chromatography is judged to be the only acceptable primary separation method. Capillary GC is preferred over packed GC. The injection system, type of liquid phase, column dimensions and operating conditions should not be specified, but performance should be maintained within established criteria.

Electron impact mass spectrometry is the primary detection candidate. Operating conditions (SIM, full-scan, or limited mass scan), performance criteria, and other variables are still to be specified. Other detection options, ECD and HECD are considered too nonspecific for these matrices or too uncommon for general application (NCIMS, MS/MS, FTIR).

Separation

As clearly evidenced in the review of the literature, GC is by far the most popular technique for PCB determination. The relative merits of PGC and CGC are well-known and apply to the separation of PCBs. CGC provides better resolution, retention time precision, and higher qualitative reliability. PGC yields a simple chromatogram (less data reduction), permits higher sample loading (and therefore possibly lower LOQs), and is generally considered easier to use. Historically, PGC quantitation has been more precise, although it has not been established how much of the imprecision attributed to CGC was due to poor technique on the part of the analyst.

The high resolution of CGC is not required in this application for separation and identification of the individual PCB congeners since the final result needed is total PCB. However, the high resolution of CGC should aid the analyst in separating PCBs from interferences. In this respect, CGC is preferable. In many cases when the sample is amenable to "dilute and shoot" techniques, very high levels of matrix materials may be present, which will overload the column. Although CGC is more sensitive to column overloading, both CGC and PGC will overload with percent levels of matrix materials. The advantages of CGC, therefore, make it the technique of choice. However, PGC should also be allowed.

Nearly every GC phase has been reported in PCB analysis. The most satisfactory separations have been achieved on nonpolar and semipolar phases (Apiezon L, methyl silicone, Dexsil, etc.). Since enforcement of very specific column parameters is difficult and since rigorous stipulations do not appear warranted, it is recommended that any nonpolar and semipolar capillary column be permitted.

The choice of CGC injector (split, splitless or "Grob," and on-column) can substantially affect the amount of material transmitted through the system. Since enforcement of use of a particular injection would be difficult and since no clear choice is presented, any injector which meets performance criteria should be permitted.

As part of the quality assurance program, a set of GC performance criteria should be established. The criteria should include number of effective plates, separation number (Tz), resolution, and peak asymmetry. Since PCBs are neutral, the acid/base characteristics of a column are of little interest; however, some measure of compound transmission through the system must be used. This may be achieved by monitoring the overall system response. Other options would entail additional work and are thus less favored.

Detection

The electron capture detector is the most sensitive candidate detector. However, it suffers from large differences in response factors for PCB congeners, which would result in very poor precision (Tables 3 and 4). Even more serious is its lack of specificity. Since many of the sample matrices will contain large amounts of halogenated nonPCB compounds, ECD would be overloaded throughout much of the chromatogram, making PCB identification and quantitation impossible. In certain cases, ECD may be a satisfactory detector, especially as a semiquantitative technique for screening samples prior to CGC/EIMS analysis.

Electron impact mass spectrometry (EIMS) appears to be the method of choice. Mass spectrometry has sufficient selectivity that a chlorinated organic matrix will not generally interfere with PCB determination. While the EI mode is not the most sensitive (NCI is much more sensitive), it is the most common ionization technique for GC/MS and, most importantly, is the most reproducible quantitatively. The precision of the EIMS depends upon the precision of the response factors. The most thorough evaluation of PCB response factors

(Martelli et al., 1981) found up to ± 20% RSD in selected isomers of one homolog. Since only 45 of the 209 congeners were characterized, the magnitude of the variation in the remaining response factors is not known.

DATA REDUCTION

Qualitative

Since most matrices subject to regulatory analysis contain substantial amounts of halogenated compounds in addition to PCBs and since an "Aroclor pattern" will not usually be present, identification of PCBs is very important. Any misidentification of a nonPCB as a PCB will yield an erroneously high value. From the EPA's viewpoint, this poses no regulatory problem. However, it may result in needless effort and cost to the regulated manufacturers.

In most cases, the EIMS data should provide sufficient confidence in the identification of PCBs for action. For those laboratories which choose to employ an equivalent technique for routine analysis, any samples with PCB values near the regulatory cutoff ("near" has not been defined) would have to be reanalyzed by the primary technique before a regulatory decision could be made.

In cases where there are some doubts as to the identity of a peak as PCB by CGC/EIMS, any available confirmatory technique should be allowed, provided that the LOQ is equivalent to or lower than the CGC/EIMS LOQ. Positive confirmations present no regulatory problems to EPA. Any confirmations which show that a peak is not PCB must be well-documented with appropriate QA (for example, a spectrum of a PCB standard spiked into the matrix). In many cases, instrument responses are highly dependent on the matrix, so the response to standards in clean solvent cannot be equated with the response in the sample.

In cases where a peak is shown to contain both a PCB and an interference, regulations should state that the entire peak must be quantitated as PCB unless the level of the interference can be precisely shown.

The qualitative criteria for the EIMS data should address the following points:

1. Full spectra
    a. Number of ions which must be present.
    b. Background subtraction techniques permitted.
    c. Ion intensity tolerances.
    d. Relative retention time windows.
2. SIM
    a. Number and mass of ions to be monitored per homolog.
    b. Tolerance of ion intensity ratios.

c. Relative retention time windows.

d. Signal-to-noise ratio.

3. LMS

a. Mass range to be scanned.

b. Tolerance of ion intensity ratios.

c. Relative retention time windows.

d. Signal-to-noise ratios.

Quantitative

Assuming that GC/EIMS is to be used, digitized data will be obtained for use in quantitation. The areas or intensities of individual mass ions must be measured, compared with those for a standard, and converted to a concentration value. This process is complicated in PCB analysis by several factors:

1. Previous schemes based on Aroclor standards are not applicable to incidentally generated PCBs.

2. PCBs are a complex mixture, so the problem really involves up to 209 separate quantitations.

3. All 209 congeners are not available as standards.

4. Two or more congeners may co-elute.

The ions for quantitation, selection of standards, and calculation procedures are discussed below.

Quantitation Ions--

The highest signal-to-noise ratio and therefore precision is a compromise between absolute ion intensity and background signal. Most analysts have chosen an ion in the molecular cluster for quantitation. Even though other ions may be more intense, the molecular cluster is at the highest mass and the background is generally lower. The use of the most intense ion in the molecular cluster is recommended for quantitation, with options of less intense ions from that cluster if interferences are encountered for the primary ion.

Calibration--

Four calibration methods are available: external standard, internal standard response factors, internal standard multi-point calibration, and direct use of the surrogates.

External standard calibration--Calibration of the analysis system versus an external standard and then quantitation using the absolute intensities or areas of the peaks lacks precision (Haefelfinger, 1981) and is not recommended for gas chromatographic analysis. Often, the greatest source of imprecision is the reproducibility of injection volume.

Internal standard response factors--In this method, internal standard(s) are added to the sample extract immediately prior to the instrumental determination, and the analytes are quantitated using the ratio of the peak height or area of the analyte and internal standard. A previously determined response factor (essentially a two-point calibration curve, with an assumed intercept at the origin) is used in converting the response ratio to mass.

For PCBs, which can span a large chromatographic range, three or four internal standards are recommended since the precision of the response factors, and therefore the final quantitation, is related to how close the analyte peak and internal standard elute (Haefelfinger, 1981; Bickford et al., 1980). Other factors to be considered in the selection of internal standards are chromatographic resolution from analytes and interferences, different mass spectral properties to assure identification in GC/MS analysis, chemical similarity to analytes (to minimize effects of changes in system selectivity), very low probability of occurring in samples, and chemical stability. Candidates for internal standards in PCB analysis include other halobiphenyls (e.g., fluorononachlorobiphenyl or dibromobiphenyl), related haloaromatics (e.g., chloronaphthalenes), and isotopically labeled PCBs (e.g., d_6-3,4,3',4'-tetrachlorobiphenyl). Given the complexity of the matrices in which by-product PCBs may need to be determined, related chloroaromatics should not be used and halobiphenyls must be selected judiciously.

Since this technique is in essence a one-point calibration, the response factors must be determined at a concentration close to that of the analyte. Differences of more than one order of magnitude may induce significant error.

Recovery surrogates added prior to any sample treatment may also be quantitated against the internal standard and, since the amount added is known, their recovery can be calculated. Knowledge of the percent recovery is useful in monitoring extraction/cleanup performance. The final number reported may be corrected for recovery if desired (or required), or the value found and percent recovery reported separately. It should be noted that if the recovery surrogates and analytes are not, in fact, equally recovered, then the reported recovery is meaningless. This will happen if the surrogates are not fully incorporated into the matrix.

Internal standard multi-point calibration--This technique is essentially the same as the response factor technique, above, except multiple calibration points (typically three, spanning up to two orders of magnitude) are used to establish a calibration curve. This has the potential for greater precision, but requires much more time and several solutions. In cases where detector sensitivity (signal response versus amount or concentration) is either nonlinear or the curve does not intercept close to the origin, a multi-point curve is advisable.

Surrogate calibration--Surrogates may be used as internal standards for quantitation. Using previously determined response factors (or calibration curves), the response ratio of the analyte and surrogate, and known masses and volumes, the mass of the PCBs may be calculated. When the surrogate recovery is less than 100%, this method automatically corrects for this loss and provides a built-in recovery correction. This method has the advantage of simpler calculation and requires fewer solutions. This technique is often referred to as isotope dilution. As with the internal standard technique, the surrogates must be incorporated into the matrix to assure equivalent recovery between the surrogate and analyte.

Selection of Compounds for Calibration--

Clearly, most of the reported quantitation methods which rely on relation of the sample peaks to those in an Aroclor standard are not applicable to by-product PCB determination.

The options for compounds to be used in calibration are:

1. Establish and use relative responses for all 209 congeners.

2. Establish and use relative responses for all available (about 80) congeners and extrapolate the responses for the other isomers.

3. Establish and use relative responses for several congeners and extrapolate the responses for the other congeners.

4. Characterize a secondary standard using all available congeners. The secondary standard would be prepared from commercial mixtures to span the range of congeners.

Option 1 is the ultimate technique. However, all 209 congeners are not available and synthesis/acquisition would be extremely expensive and require well more than a year for completion. Thus, even if this approach is to be pursued, an interim approach must be specified. Options 2 and 3 are compromises. Option 2 could be termed the best available method. Option 3 is easier to implement and utilizes a reasonable number of quantitation congeners. Option 4 would generate a well-characterized mixed Aroclor or similar mixture. This has the advantages of low cost (once the characterization has been completed) and uniformity. The disadvantages are that (a) the concentrations of the congeners range over two or more orders of magnitude, so calibration of the instrument would be difficult and (b) many users will have only a limited range of PCB homologs (e.g., only dichlorobiphenyls) and would not want to use a standard requiring a full GC temperature program.

Options 2 and 3 appear to be the most applicable. Whether Option 2 or 3 is more appropriate depends on the variability of the response factors and the precision desired by EPA. This area needs to be further investigated.

Assuming that all 209 congeners are not characterized and used as calibration standards, analysts will have to extrapolate response factors from the standards used to other isomers. Guidelines for these extrapolations must be specified. A preliminary investigation by at least one laboratory to define the response factor variability among all available congeners is recommended. An estimate of the error associated with the extrapolation would be available from statistical evaluation of the resulting data.

LIMIT OF QUANTITATION

Extrapolation of the data in Table 2 to a proposed LOQ for the PCB Remand Rule is difficult because of several uncharacterized variables. The levels of interferences will vary widely. In addition, recoveries will vary, also affecting the LOQ. A major variable is the concentration factor in the workup (number of grams of sample concentrated or diluted to a given sample volume for injection on the GC). If the method works with a 1-g sample, an order of magnitude decrease in LOQ can be effected by using a 10-g sample. This requires additional effort and therefore cost. Taken to the extreme, it is possible to use very large samples (many kilograms) to lower the LOQ. On the other hand, the customary volume to concentrate a sample extract is 1 ml. One can, with some difficulty and loss of volume precision, further concentrate the extract to 100 µl, effecting a 10-fold decrease in LOQ. However, if the sample is still dirty, this further concentration can lead to solidification, which prevents injection onto a GC column.

DATA REPORTING

The final data report should list total PCB as the bottom line number, since this is the value of regulatory interest. The analytical reporting format should be specified to eliminate any ambiguity and should address the following issues:

1. Tabulation of individual congener quantitation. This may be difficult to achieve since congener identifications may not be available for more than a few congeners.

2. Tabulation of individual homolog quantitation. This should be required so that data reviewers can assess the data.

3. Reporting units. These must be specified. Units such as micrograms per gram (solids), micrograms per liter (water), and micrograms per cubic meter (air) are recommended.

4. Recovery correction. If the final protocol specifies use of surrogates to monitor recoveries and if the method is validated, then recovery correction would be appropriate. While this conflicts with the customary practice in pesticide residue, priority pollutant, and other analyses, it is consistent with the practice in many other fields (e.g., clinical analyses). Since near quantitative (> 70%) recovery cannot be assumed, recovery correction is strongly recommended. Although high recoveries may not be guaranteed, very low recoveries cannot be tolerated. The lower the recovery, the higher the overall method LOQ. In addition, very low recoveries are generally accompanied by poor precision. If, for instance, 10 ± 5% recovery is achieved, the uncertainty in the nominal 10X correction factor is huge (6.7-20X). Thus, a lower acceptable limit of recovery (e.g., 30%) must be stipulated for acceptable data.

5. Standard reporting format. A standard reporting form, including all equations to be used, intermediate calculations, etc., should be required. This improves quality assurance since the chance for error (e.g., using the

wrong conversion factor) is reduced, and any errors would be detected more easily. In addition, data presented to regulatory personnel on standard forms are much easier to review.

6. Internal standards. If no recovery surrogates are available, internal standards would most certainly be advocated. Their use generally improves precision, and thus data quality, over the use of external standards. If surrogates are used, the need for internal standards is not so clear. One can use the surrogate response in the calculation of unknown concentrations. In this case, instrument response variability, losses in the instrument, and workup recovery are taken into account, all in one calculation. Thus, recoveries are corrected without any real knowledge of the percent recovery. On the other hand, the use of both internal standards and recovery surrogates would yield a fairly accurate assessment of the recovery and permit the analyst (or regulator) to decide if the recovery is unacceptably low. While knowledge of recoveries is not of central regulatory concern, it does provide the analyst with an estimate of the method performance. Therefore, if no internal standards are used, a semiquantitative estimate of recovery must be made using the CGC/EIMS response (area counts or similar measure) to the surrogates. If this is below a certain threshold (say 30% of expected), then the sample preparation must be repeated or changed. The use of the surrogate compounds as standards for both workup and instrumental analysis is simple; and since it is one step instead of two, it should be more precise. The price paid for this simplicity is that recoveries are not well characterized. In the interest of simplicity and better precision, the use of internal standards in addition to recovery surrogates is not recommended.

CONFIRMATION TECHNIQUES

Qualitative

Alternate columns, detectors (HREIMS, FTIR, NCIMS, HECD, etc.), and techniques such as MS/MS, direct probe HREIMS, NMR, FTIR, HPLC, etc., will be permitted for confirmation of PCBs. Proper validation and demonstration of comparable or lower detection limit must be provided with any confirmation which overrules the GC/EIMS identification and eliminates the compound from quantitation as a PCB.

Quantitative

As part of the overall QA, quantitative confirmation is required. The options proposed include duplicate analyses and standard addition. Acceptance criteria for these confirmatory techniques are discussed in more detail in the Quality Assurance subsection.

SCREENING/EQUIVALENT METHODS

Alternate procedures to the designated protocol may be necessary to obtain rapid estimates of PCB concentration for commercial facilities operating on a continuous process basis or for small businesses relying on contract laboratories for analyses. The alternate procedures could possibly include perchlorination, dechlorination, TLC, PGC/ECD, PGC/HECD, CGC/ECD, CGC/HECD, etc.

The data generated by these methods would be for the individual industry's use to determine if changes in process design or initial reactants are necessary to lower the levels of PCBs in the final product.

However, compliance with the regulations must still be determined with the designated protocol unless EPA accepts the screening technique as equivalent to the protocol.

Equivalency must be demonstrated in terms of sensitivity and selectivity for PCBs, limits of detection and quantitation, and interferences. A strong QA program must be implemented to establish and monitor the equivalency of an alternate method. The quality control program should include measurements of blanks, spiked blanks, and spiked samples (blind and known) to establish limits for precision, accuracy, and recovery of analyses from the sample matrix.

Equivalent methods would be most applicable to continuous process operations with little system variance. Gross changes in any parameter of a continuous operation process should require further verification of equivalency of the alternate method. The levels of PCBs in a fraction of all samples should still be analyzed according to the proposed primary protocol for quality assurance.

SECTION 5

POSSIBLE ANALYTICAL SCHEMES

The purpose of this section is to discuss how all the analytical components presented in Section 3 can be integrated to produce an effective overall protocol.

For discussion purposes, it is presumed here that a primary protocol will be established and that it will contain the following steps:

1. Homogenize sample and subsample if necessary.

2. Incorporate surrogate compounds (e.g., four ^{13}C PCB congeners).

3. Dilute, extract, or clean up as required.

4. Concentrate or dilute to a known volume.

5. Analyze a known aliquot by CGC/EIMS.

6. Identify PCBs by relative retention time and mass spectral characteristics.

7. Integrate the PCBs by homolog and calculate amounts of each homolog by normalizing the responses to responses for the surrogate compounds, using one or more homolog response factors.

8. Sum all 10 homolog concentrations to obtain a total PCB value.

9. Report on standard reporting form.

10. Follow specified routine quality assurance (blanks, controls, duplicates, standard addition, instrument performance criteria, etc.).

11. Maintain appropriate records.

ISSUES TO BE ADDRESSED

If this or a similar protocol is specified, several issues must be addressed.

Method Flexibility

Some flexibility must be permitted in the method details (GC columns, solvent evaporation techniques, etc.) to accommodate different apparatus and laboratory practices. However, excessive flexibility will adversely affect the data quality since many operations are uncontrolled. With proper QA practices, the method can be flexible while still generating acceptable results. Thus, it appears that the best approach is to provide options and suggest rather than require for most method details. As long as the laboratory demonstrates it is within the performance boundaries specified by the QA guidelines, the optional approaches should be allowed.

Substitute Methods

Except when validated and routinely confirmed by CGC/EIMS, no substitute methods should be permitted.

Equivalent Methods

Equivalent methods should be permitted. Equivalent methods (TLC, GC/ECD, etc.) are defined as methods which have been validated against the primary method and yield comparable quantitative results and have LOQs comparable to the primary method or lower LOQ than the regulatory cutoff. Results obtained by an equivalent method must be confirmed by the primary method if significant interferences are suspected or the levels found are near the regulatory cutoff ("near" must be defined). Any use of an equivalent method would be subject to the additional QA provision that a specified number (e.g., every tenth) of samples be routinely run by the primary method and that the two results agree within specified tolerances (the agreement should be specified by homolog, not simply by total PCB, to avoid any method bias toward one end of the homolog lines).

Since an equivalent method would be subject to validation and additional QA, it would be applicable only to routine monitoring of a process. Obviously any single batches or one-shot analyses would have to be done by the primary method. The major application of equivalent methods is projected for the company with a process at several plants which must be monitored periodically. Since most plants do not have GC/MS instrumentation and a slow turnaround from central research would either delay product shipping or permit untested product to be released to customers, use of an equivalent method appears to be the only acceptable alternative.

QUALITY ASSURANCE

The QA options to be addressed include:

1. Round robins: One or more round robins appear to be a good mechanism for improving the methodology and predicting the data quality. The objectives and execution of the round robin need to be addressed. Whether periodic round robins should be required is also of interest.

2. QA organization: Some organization must be designated to administer QA. The responsibilities and authority of the organization need to be specified. At one extreme, the QA organization periodically reviews the data submitted. On the other extreme, the QA organization would have laboratory

facilities and confirm results on selected samples, prepare and send out performance audit samples, organize and execute round robins, conduct systems audits, and conduct method development efforts when necessary. Clearly the data quality and cost are roughly proportional to the amount of QA. A sensible compromise must be reached.

3. Systems audits: One standard QA practice is the systems audit. This is especially valuable in that the QA officer observes the personnel and facilities in operation and assesses their competence and performance. This is the only way the QA office can monitor the laboratory practices and review the raw data (chromatograms, mass spectra, magnetic tapes, etc.). The use of systems audits is desirable, but it requires personnel and travel fund commitments.

4. Performance audits: A performance audit is a quantitative analysis with a material of known PCB content. Performance audits consist of blanks and samples, blind or known, submitted by the QA lab and are generally analyzed along with routine samples. A performance audit system is mandatory as part of the overall laboratory certification program.

5. Laboratory certification: A laboratory certification program is recommended. The quality of the data and therefore the laboratory capabilities and performance must be assured. There are several methods for laboratory certification: round robin participation, performance audit participation, or submission to a systems audit. Most likely a combination of the three would be the most reasonable certification route. Following initial certification, all participating laboratories must be periodically recertified. Performance audits and systems audits are the most appropriate recertification methods.

APPENDIX A

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APPENDIX B

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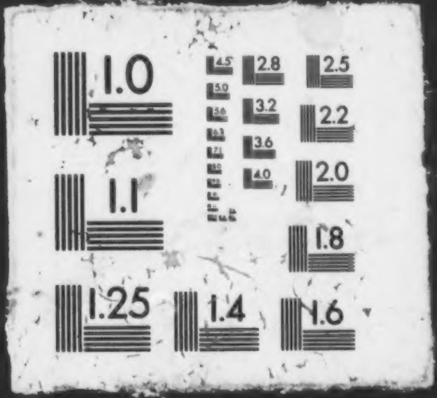
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